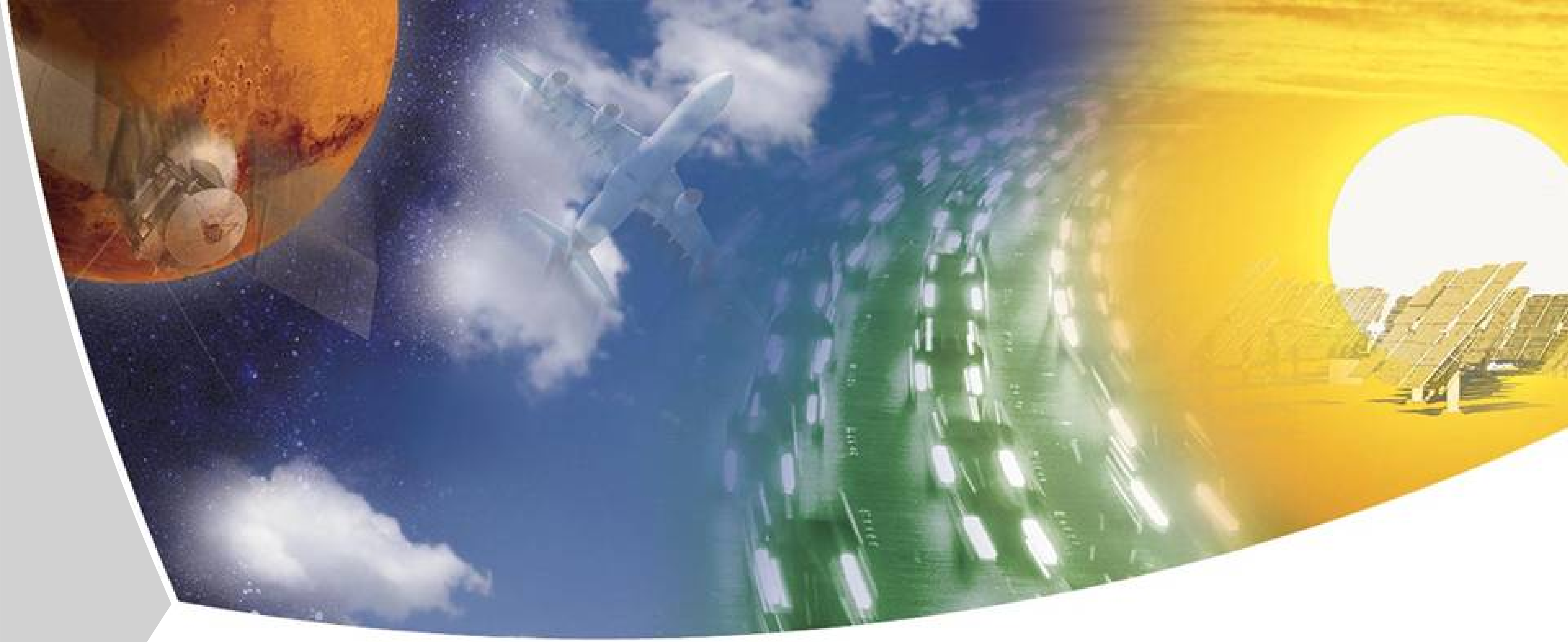

Theory and Application of Electrochemical Impedance Spectroscopy for Fuel Cell Characterization

Norbert Wagner, Andreas K. Friedrich

German Aerospace Center, Institute for Technical Thermodynamics

Pfaffenwaldring 38-40, 70569 Stuttgart

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Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

Presentation outline

- Introduction
  - Motivation
  - Types of Fuel Cells
  - Experimental set-up for different types of FCs

- Examples of porous electrodes
- Impedance models of porous electrodes

- Different applications of EIS in FC research
  - Contributions to performance loss of PEFC (single cell)
  - Time dependent EIS
    - CO poisoning of PEFC-anodes
  - EIS measured on Ag-gas diffusion electrode (half cell)
  - EIS measured on SOFC (segmented cell)
- Conclusion and Outlook
  - EIS with fuel cell stacks
  - EIS on batteries (Li-Sulfur, Li-Air (Metal-Air) for determination of kinetics, degradation, SOC, SOH

Motivation

Characterization of Fuel Cells by Electrochemical Impedance Spectroscopy:

- Determination of electrode structure and reactivity, separation of electrode structure from electrocatalytical activity
- Determination of electrochemical active surface (locally resolved)
- Determination of reaction mechanism and separation of different overvoltage contributions to the fuel cell performance loss
- Determination of degradation mechanism of electrodes, electrolyte and other fuel cell components (bipolar plates, end plates, sealings, etc.)
- Determination of optimum operation condition (e.g. gas composition, temperature, partial pressure), cell design (flow field) and stack design

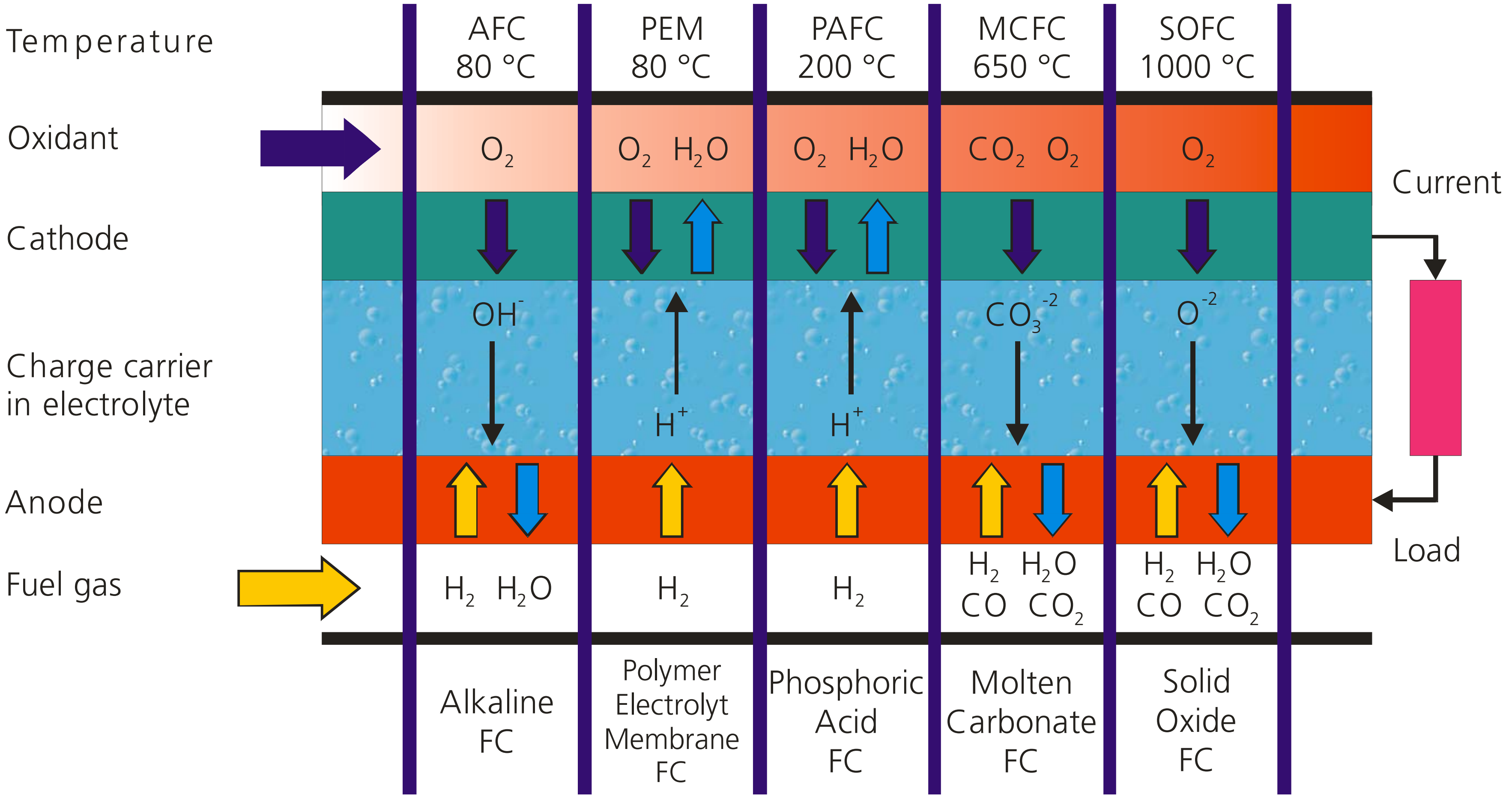
Thermodynamic Date of Selected Fuel Cell Reactions

(Standard Conditions @25 °C)

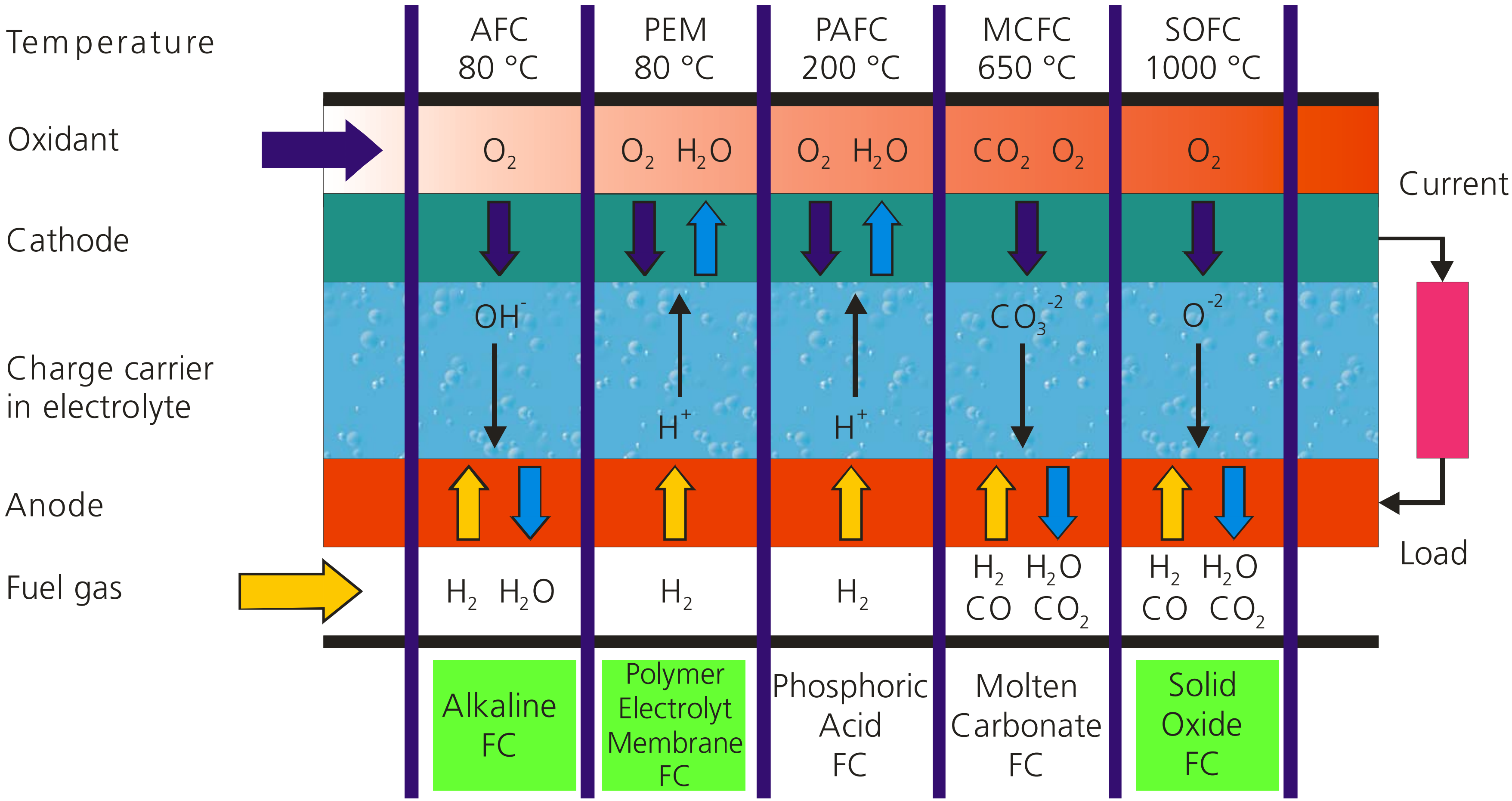
Fuel Cell	Reaction	z	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	U^0 (V)	η_{theo}
Hydrogen	$H_2 + ½ O_2 \rightarrow H_2O$	2	-286.0	-237,3	1,229	83,0 %
CO	$CO + ½ O_2 \rightarrow CO_2$	2	-283.1	-257,2	1,066	90,9 %
Formic acid	$HCOOH + ½ O_2 \rightarrow CO_2 + H_2O$ (l)	2	-270.3	-285,5	1,480	105,6 %
Formaldehyde	CH_2O (g) $+ O_2 \rightarrow CO_2 + H_2O$ (l)	4	-561.3	-522,0	1,350	93,0 %
Methanol	$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (l)	6	-726.6	-702,5	1,214	96,7 %
Methane	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (l)	8	-890.8	-818,4	1,060	91,9 %
Ammonia	$NH_3 + ¾ O_2 \rightarrow ½ N_2 + 3/2\ H_2O$ (l)	3	-382.8	-338,2	1,170	88,4 %
Hydrazine	$N_2H_4 + O_2 \rightarrow N_2 + H_2O$ (l)	4	-622.4	-602,4	1,560	96,8 %
Zinc	$Zn + ½ O_2 \rightarrow ZnO$	2	-348.1	-318,3	1,650	91,4

W. Vielstich
in Handbook of Fuel Cells Vol. 1, (W. Vielsich, H.A. Gasteiger, A. Lamm eds.) John Wiley & Sons, London, 2003

Schematic representation of main types of fuel cells

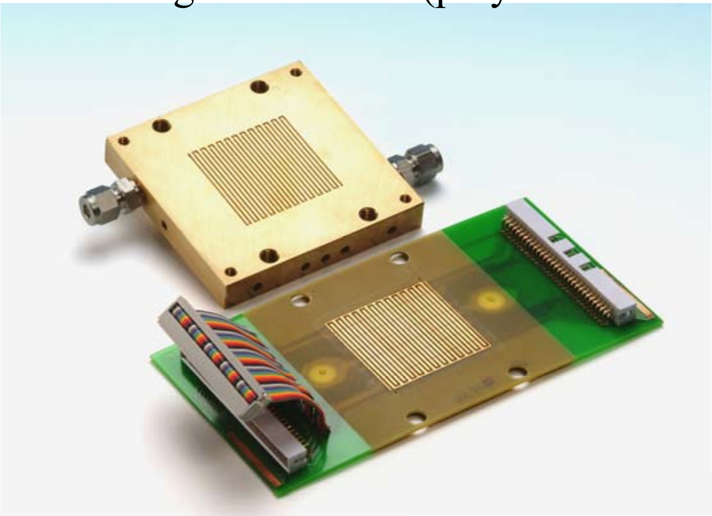


Schematic representation of main types of fuel cells

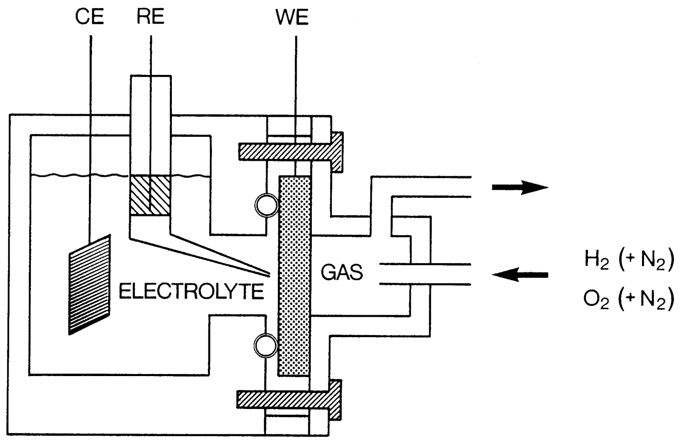


Experimental set up and cells used for EIS

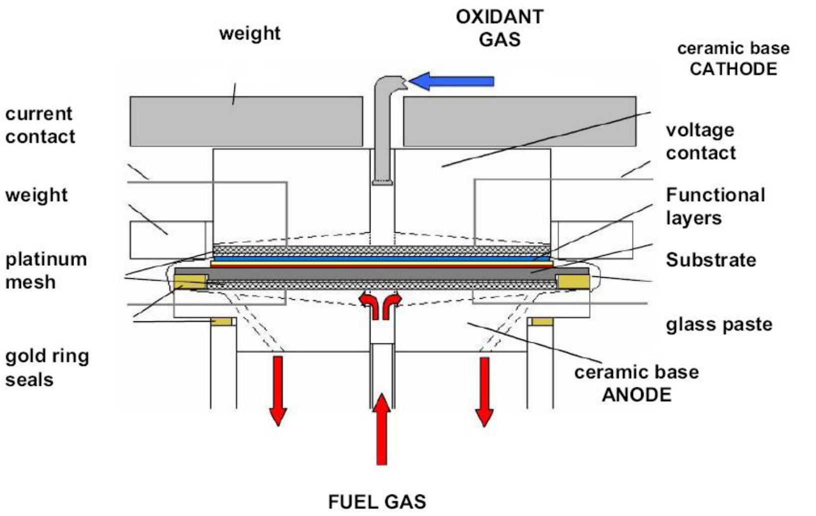
Segmented and single PEFC cell (polymer electrolyte)



Fuel „half“ cell with liquid electrolyte



Test cell for SOFC (short stack)
(Solid Oxide Electrolyte)



Fuel cell overvoltage and current density / voltage characteristic

Hydrogen Oxidation Reaction (HOR):

$\eta_{H_2} = RT/2F \; i/i^*$

Oxygen Reduction Reaction (ORR):

$\eta_{O_2/air} = RT/[(1-\alpha)2F] \; [\ln i - \ln i^*]$

Ohmic loss

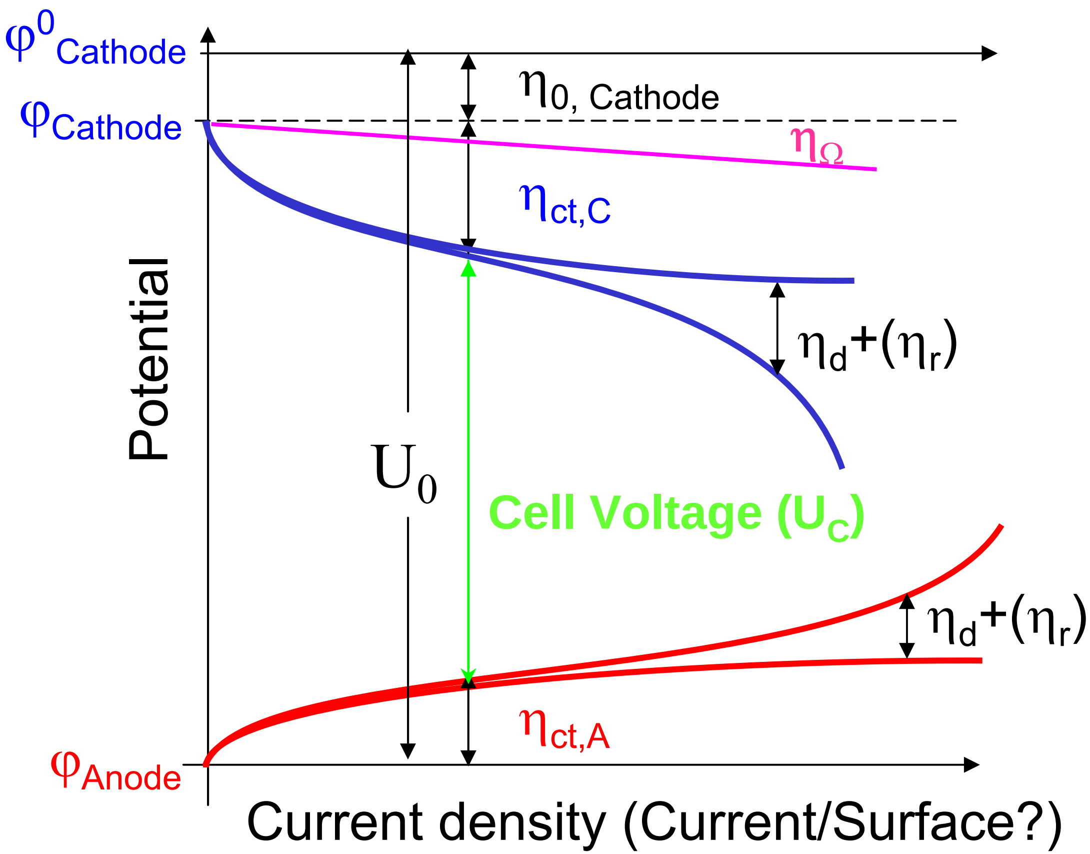
$\eta_\Omega = iR$

Transport limitation (diffusion)

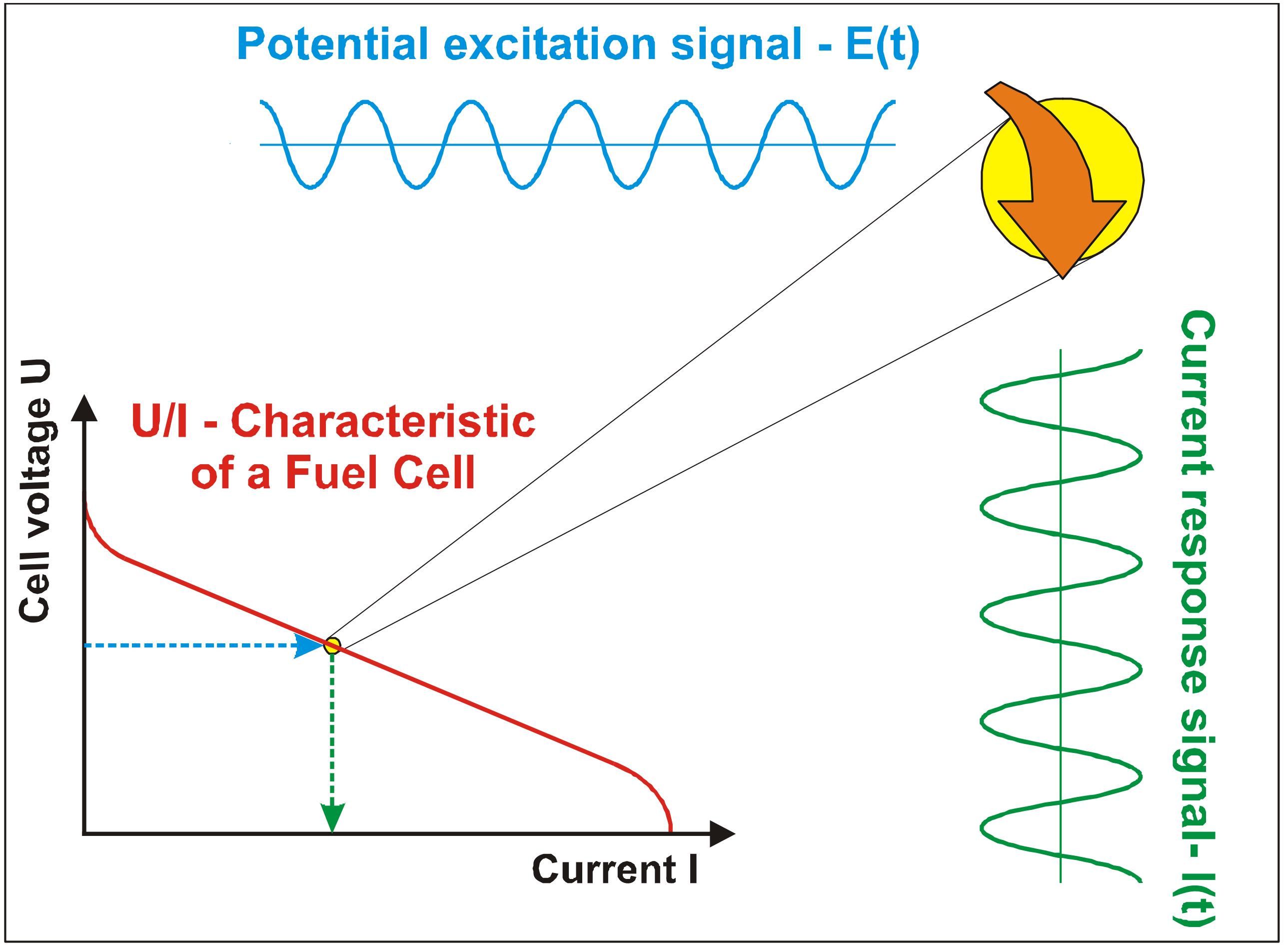
$\eta_d = -RT/2F \ln(1 - i/i_{lim})$

Fuel cell voltage

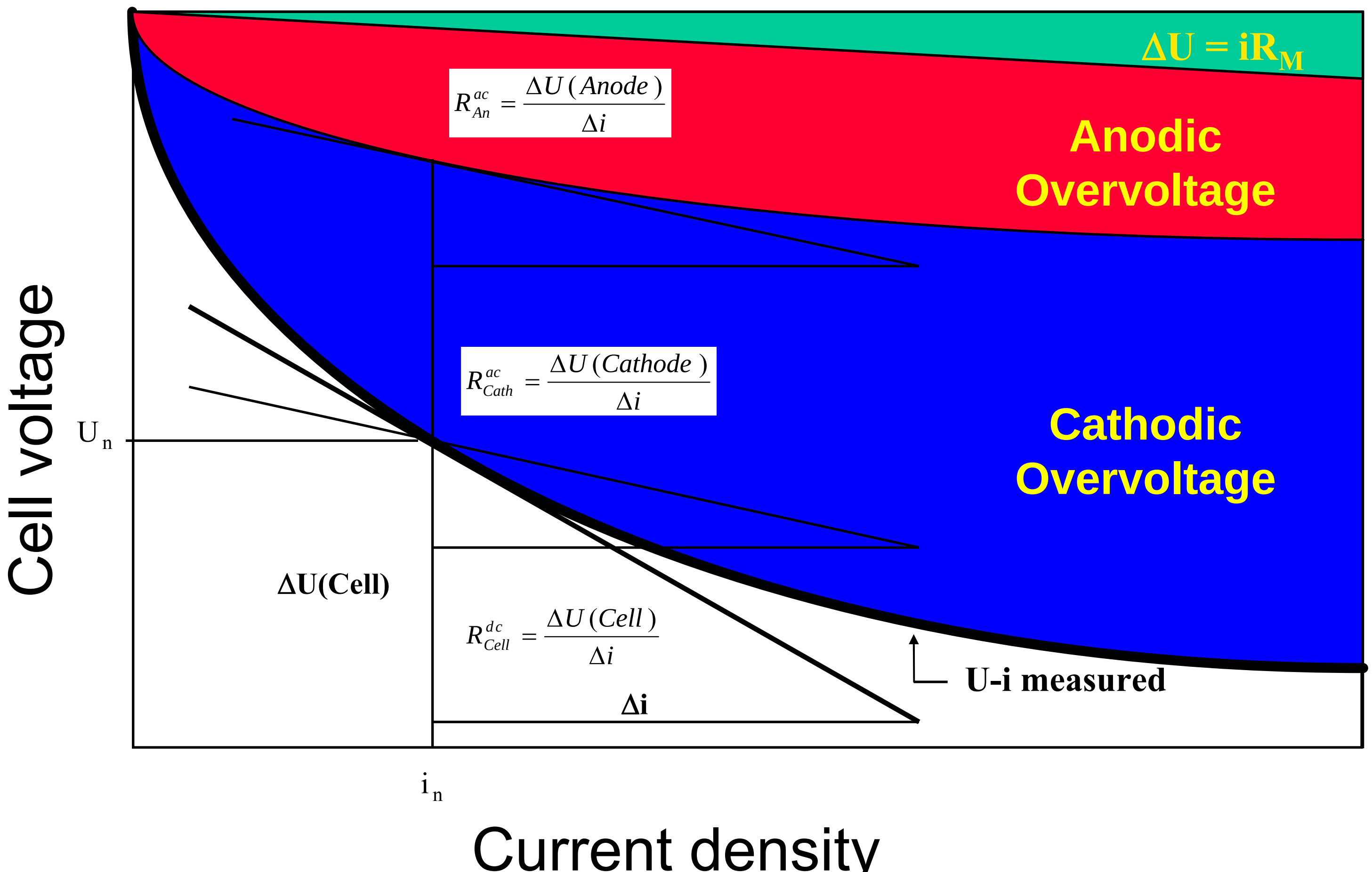
$U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega$



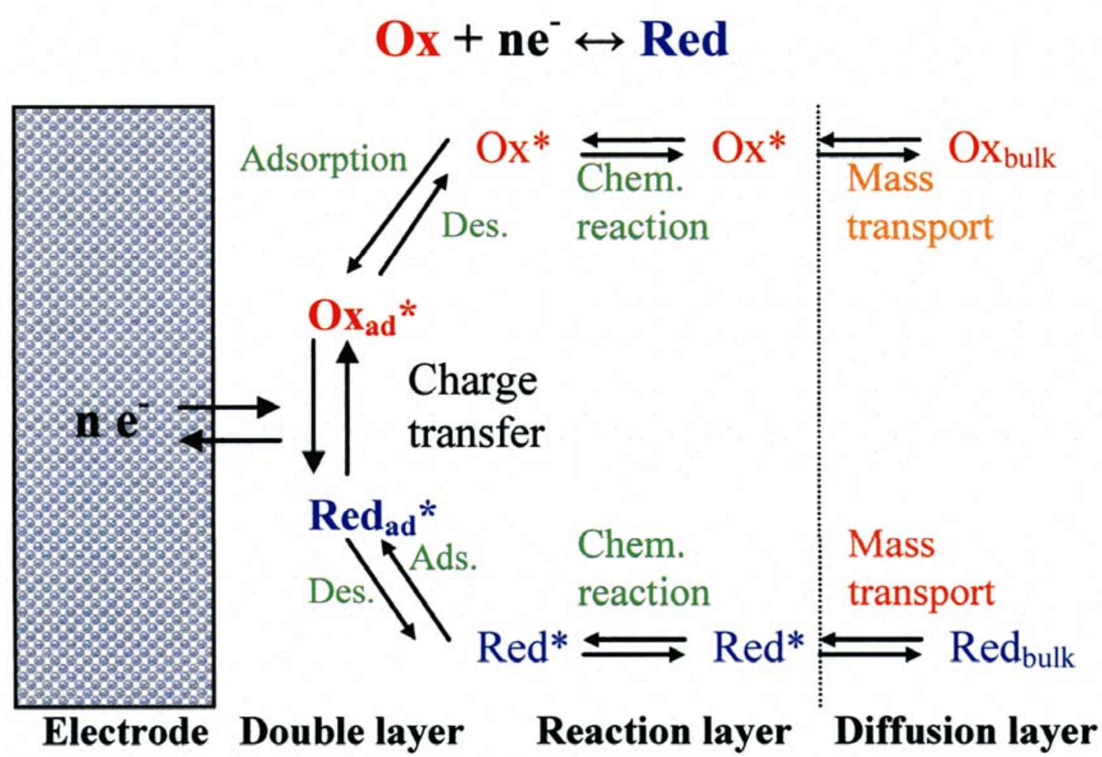
Electrochemical Impedance Spectroscopy: Application to Fuel Cells



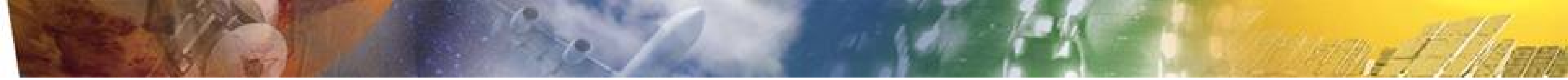
Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance Measurements



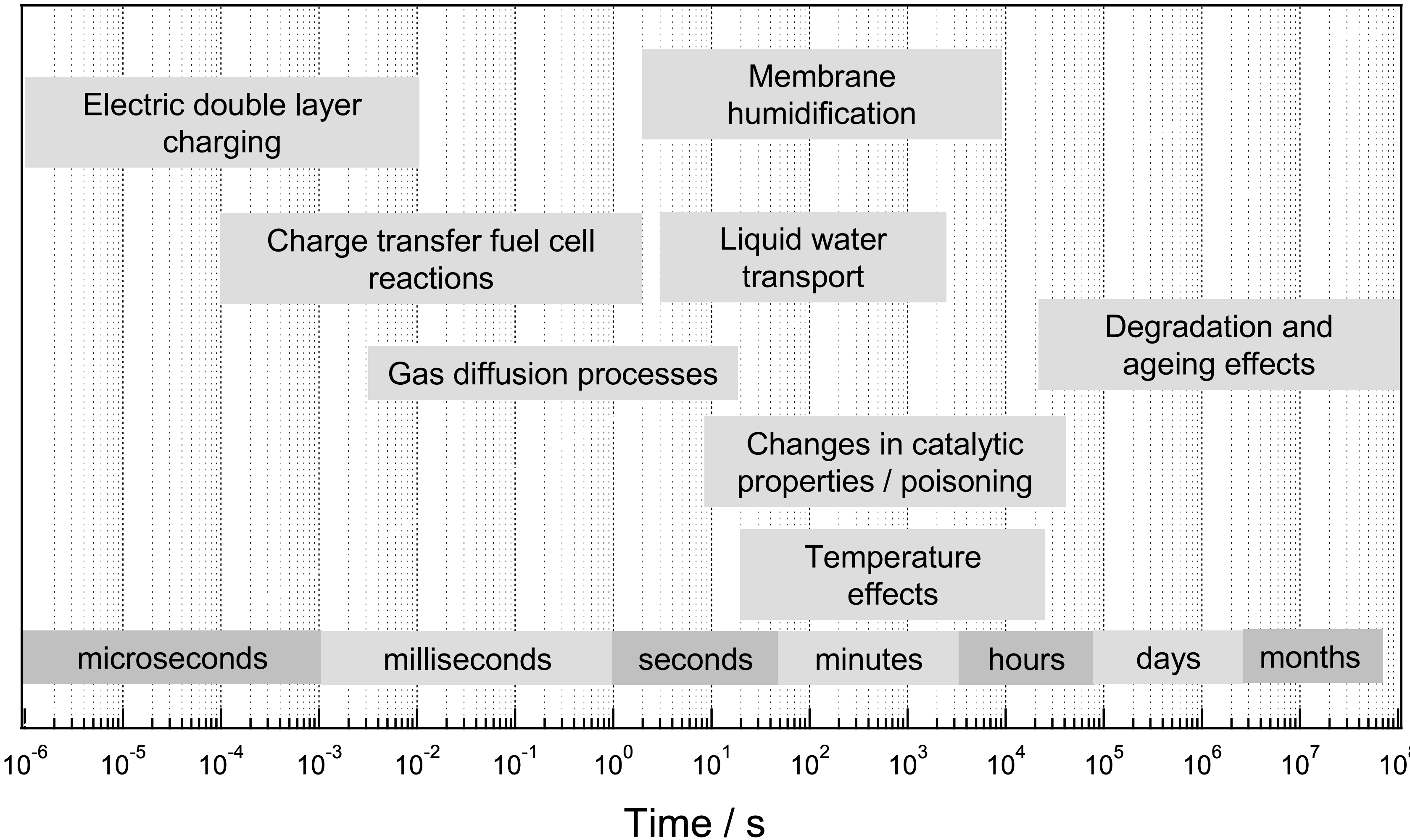
Schematic representation of the different steps and their location during the electrochemical reactions as a function of distance from the electrode surface



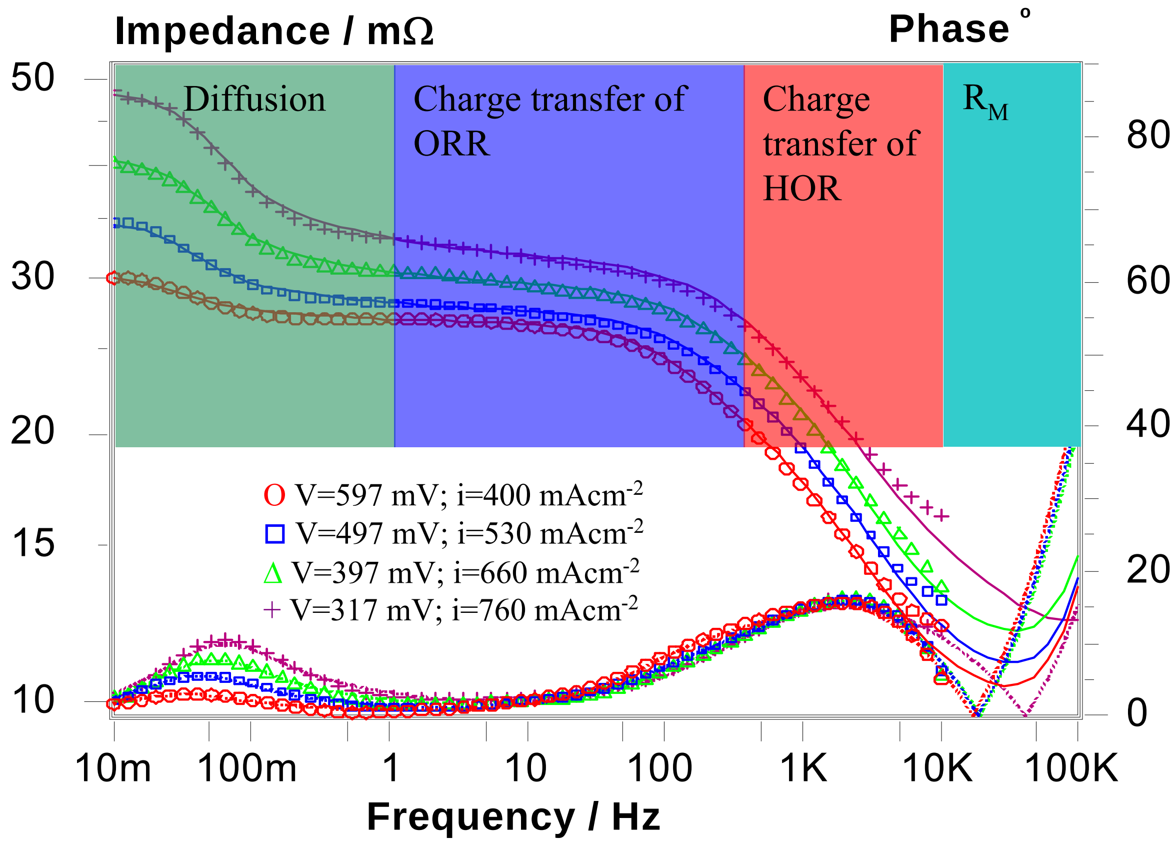
N. Wagner, K.A. Friedrich, *Dynamic Response of Polymer Electrolyte Fuel Cells* in „Encyclopedia of Electrochemical Power Sources" (Ed. J. Garche et al.), ISBN-978-0-444-52093-7, Elsevier Amsterdam, Vol.2, pp. 912-930, 2009



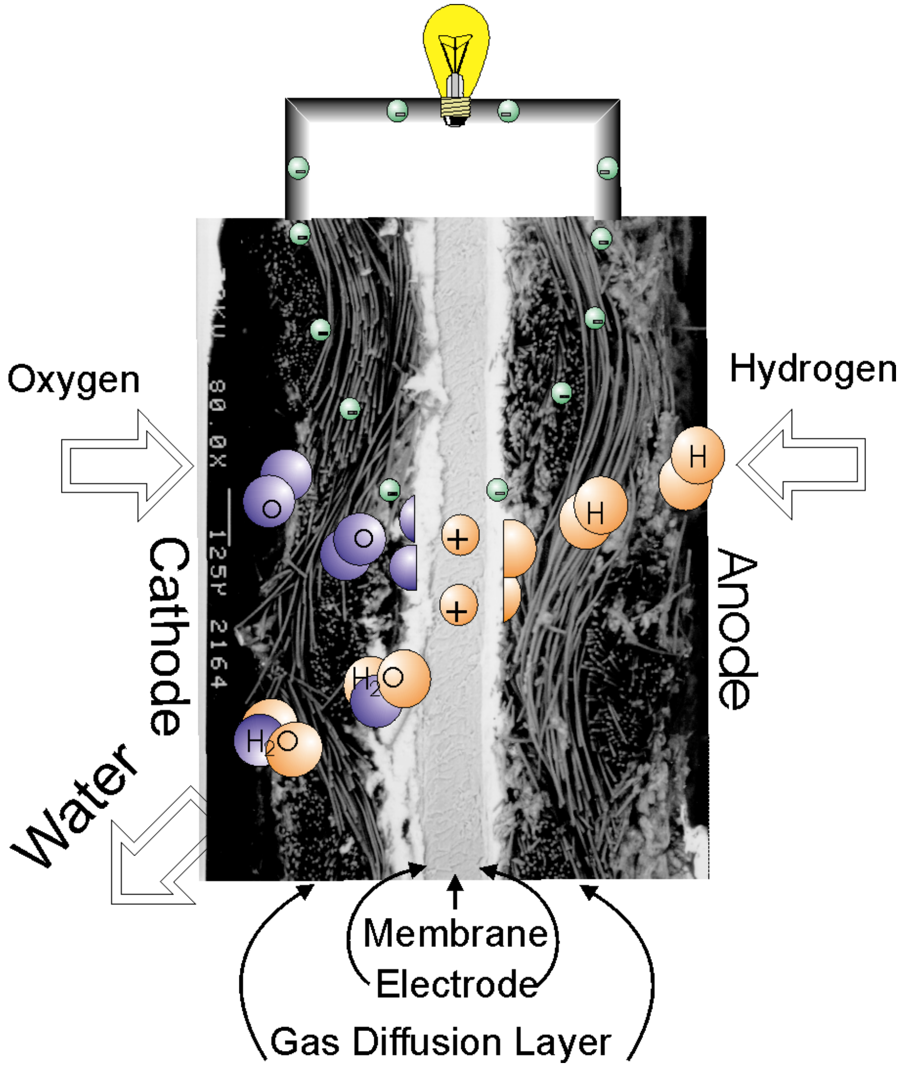
Overview of the wide range of dynamic processes in FC



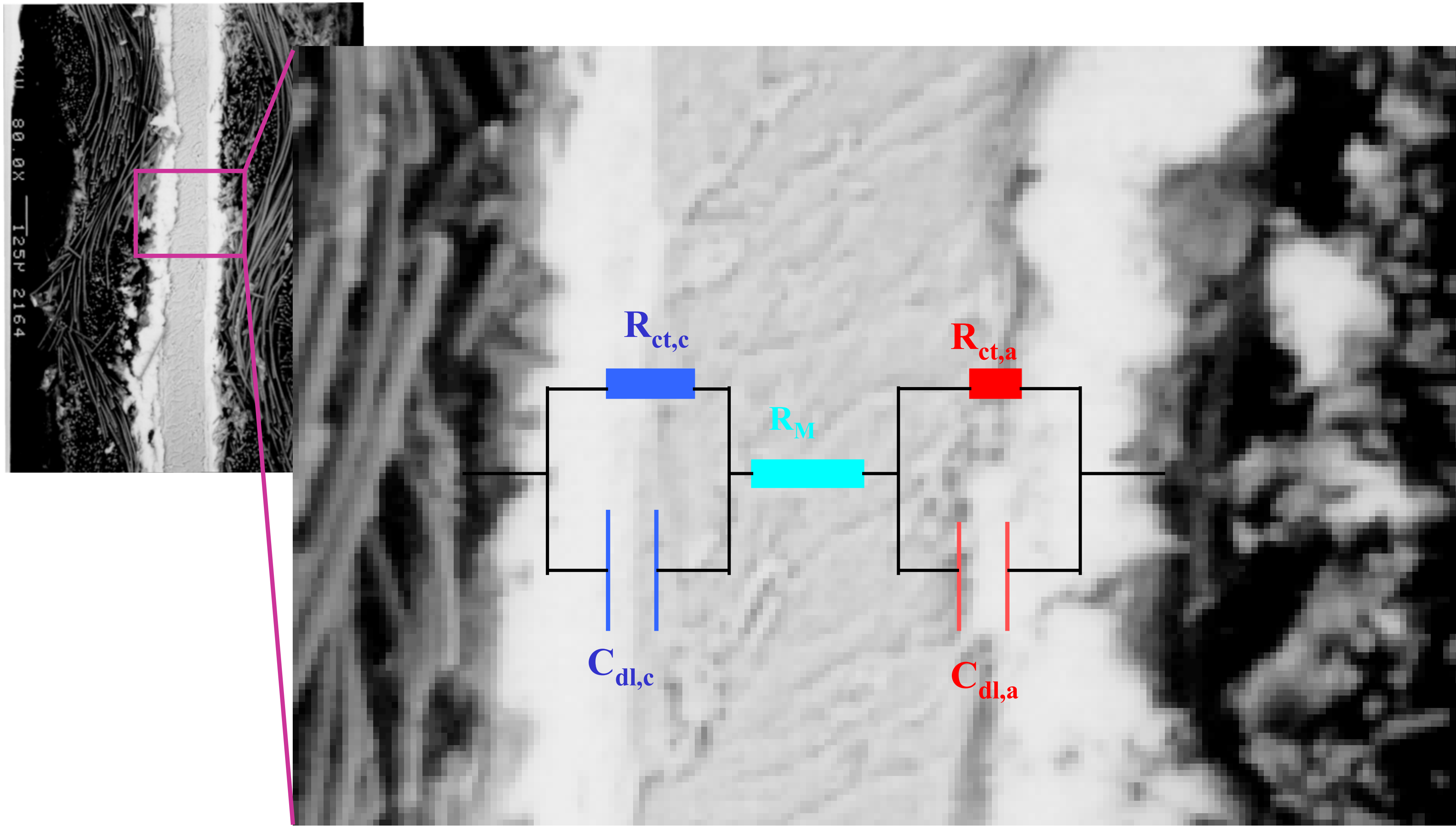
Bode representation of EIS measured at different current densities, PEFC operated at 80°C with H_2 and O_2 at 2 bar



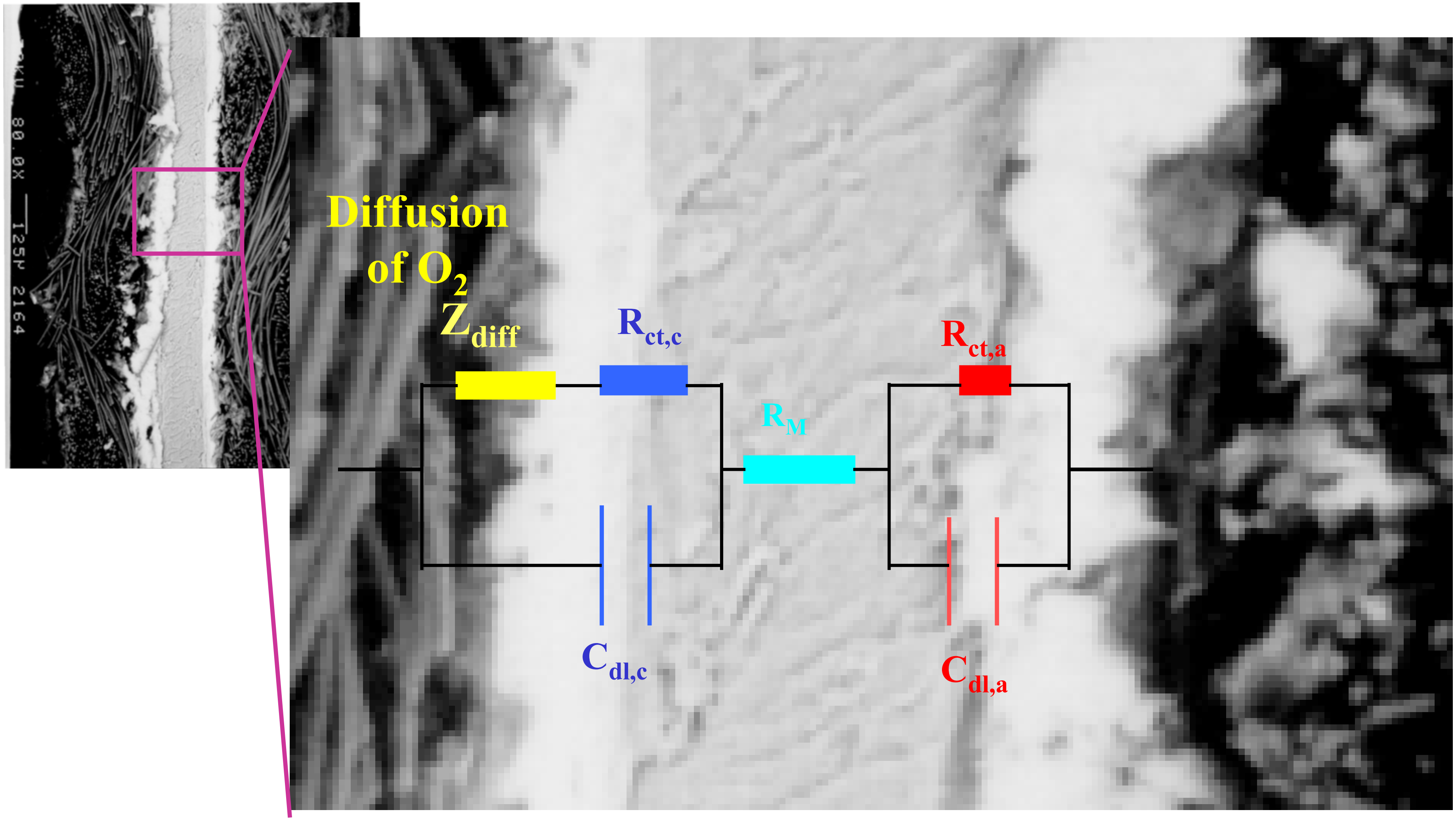
PEFC: Schematic Diagram (cross section)



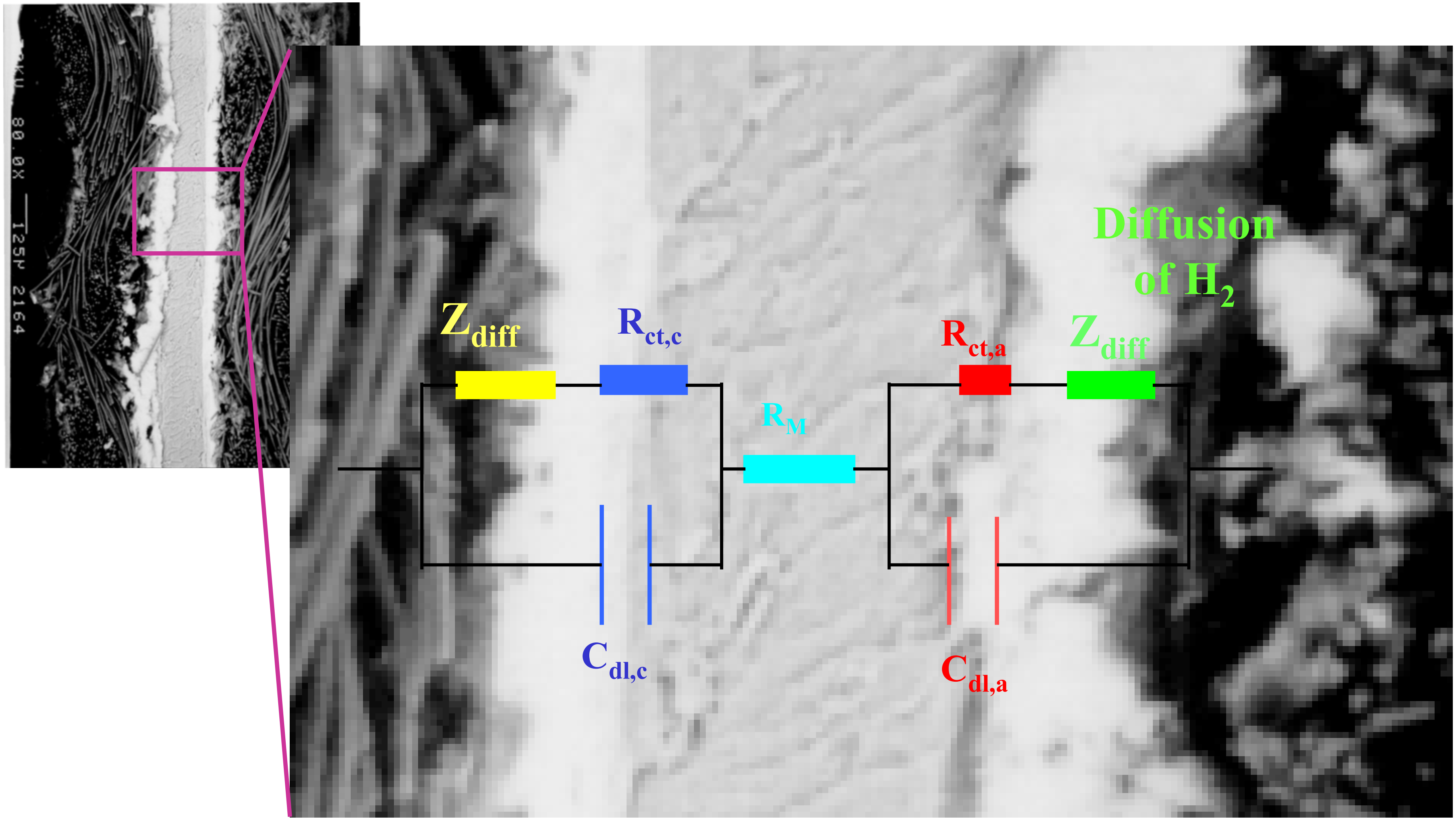
Common Equivalent Circuit for Fuel Cells



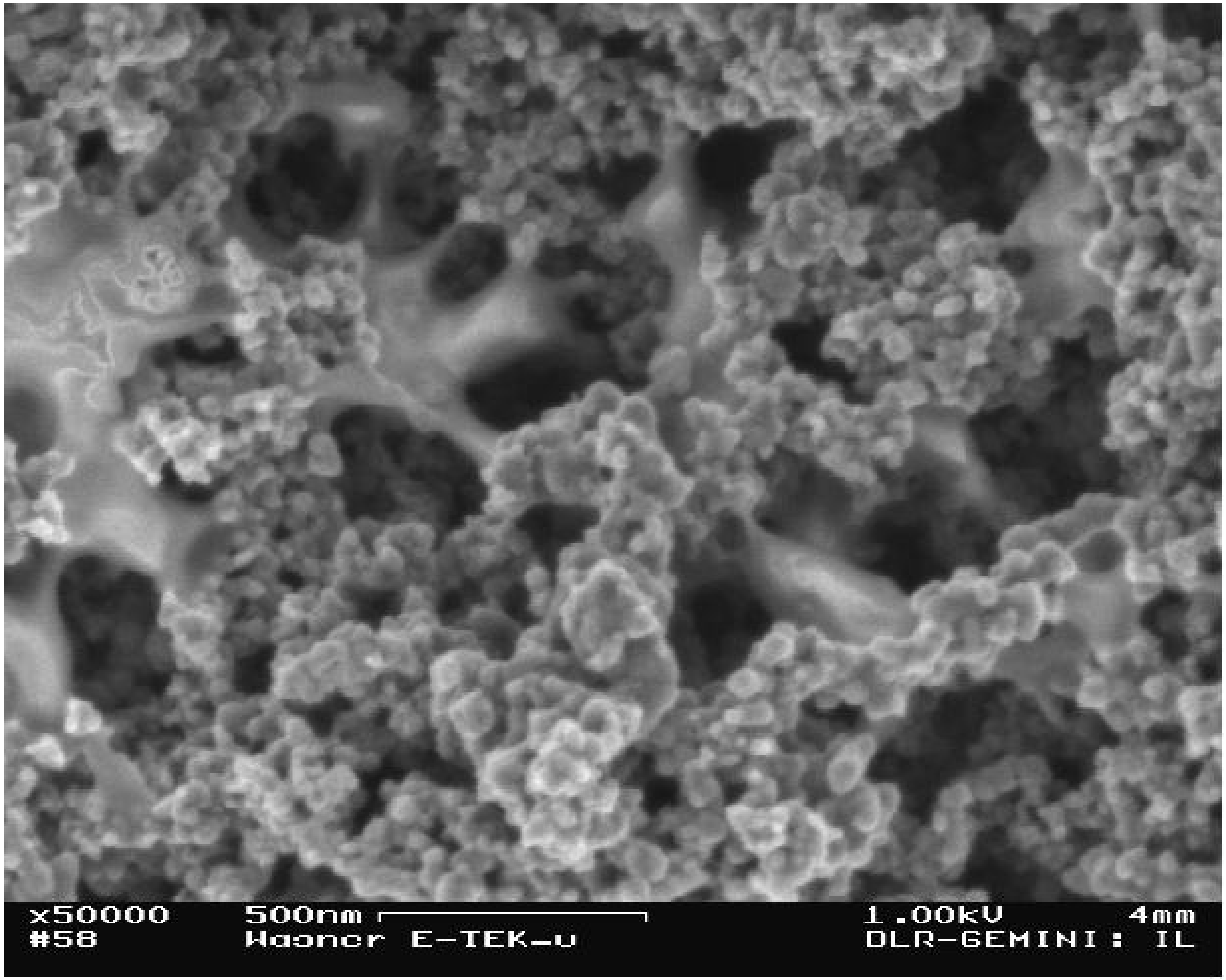
Common Equivalent Circuit for Fuel Cells



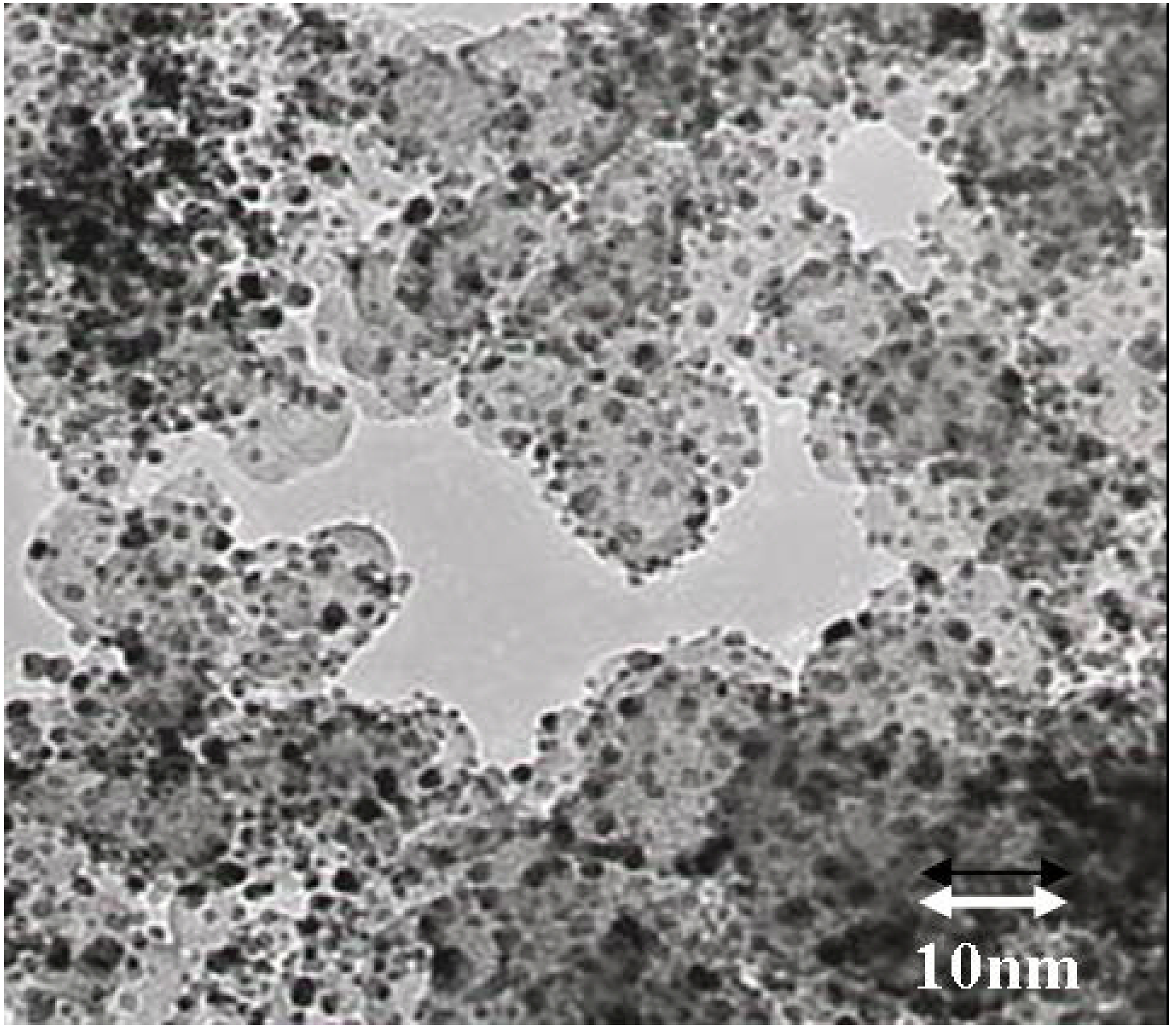
Common Equivalent Circuit for Fuel Cells



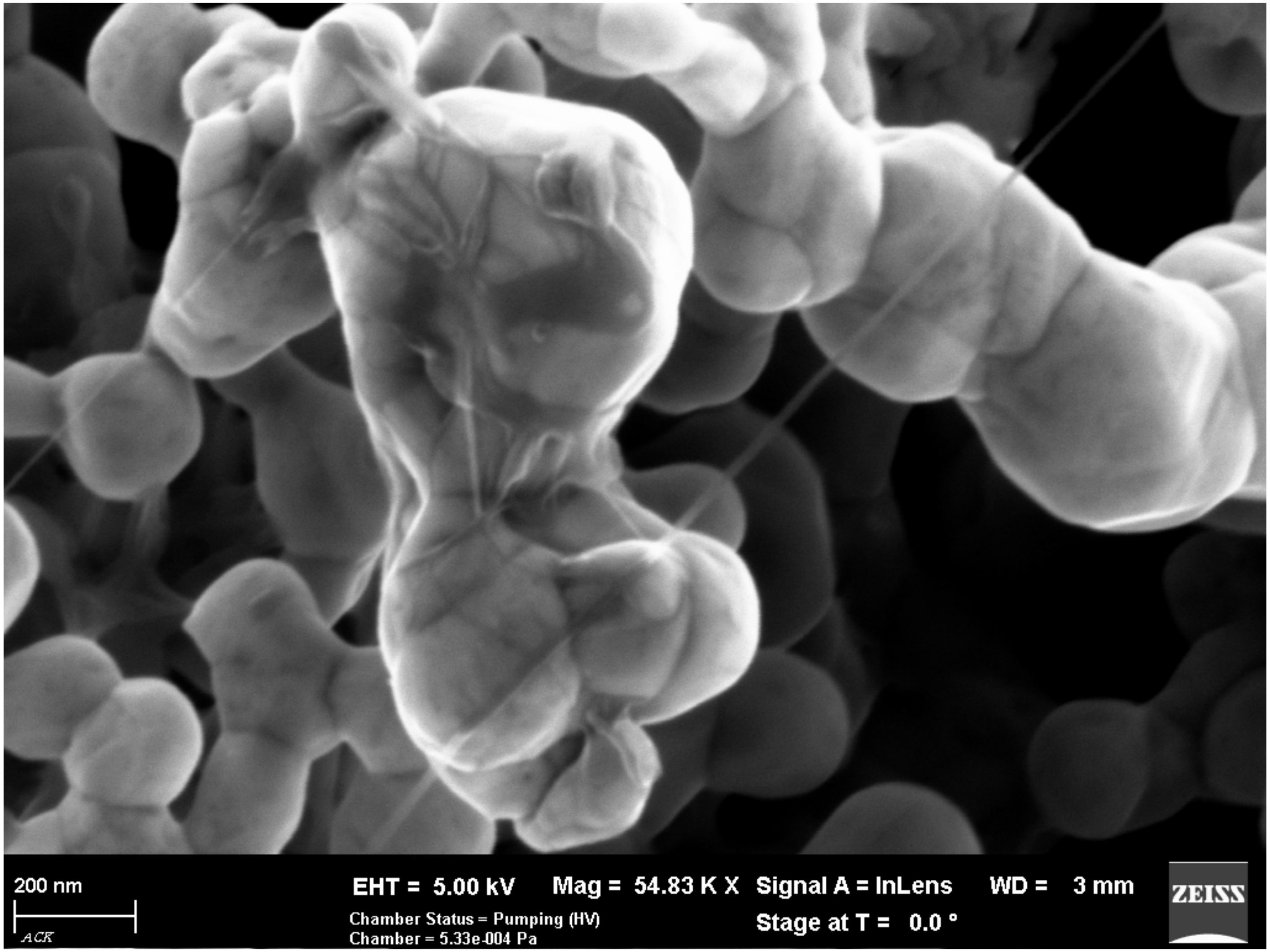
SEM micrograph of PEFC elctrode (Pt/C+PTFE)



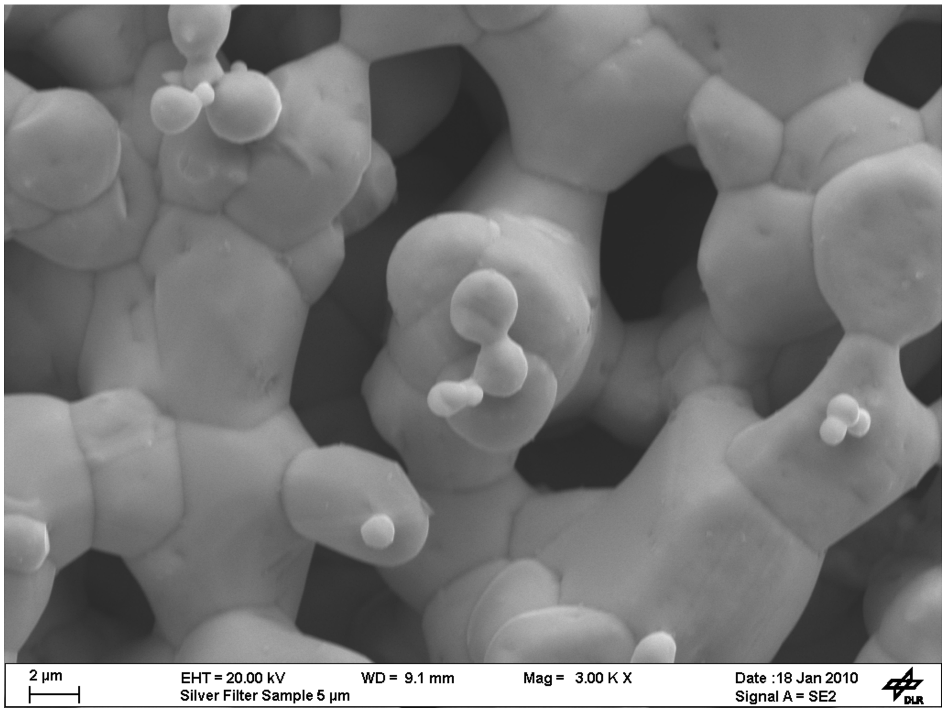
TEM micrograph of Carbon Supported Platinum Catalyst



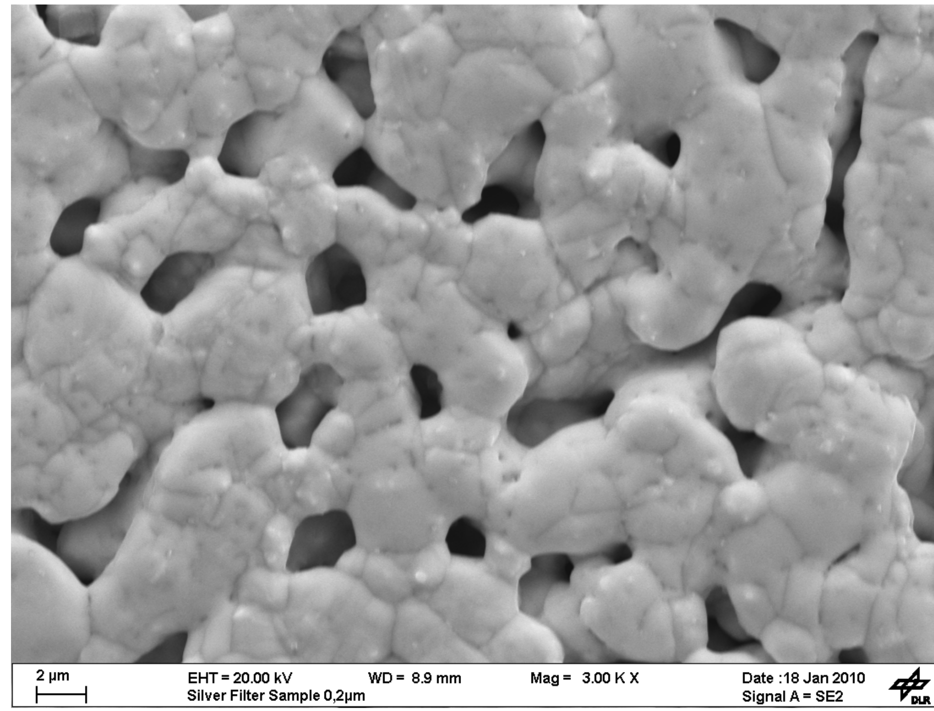
SEM-picture of Silver-Gas Diffusion Cathode



SEM-picture of a Silver membrane surface, 3 kx magnification



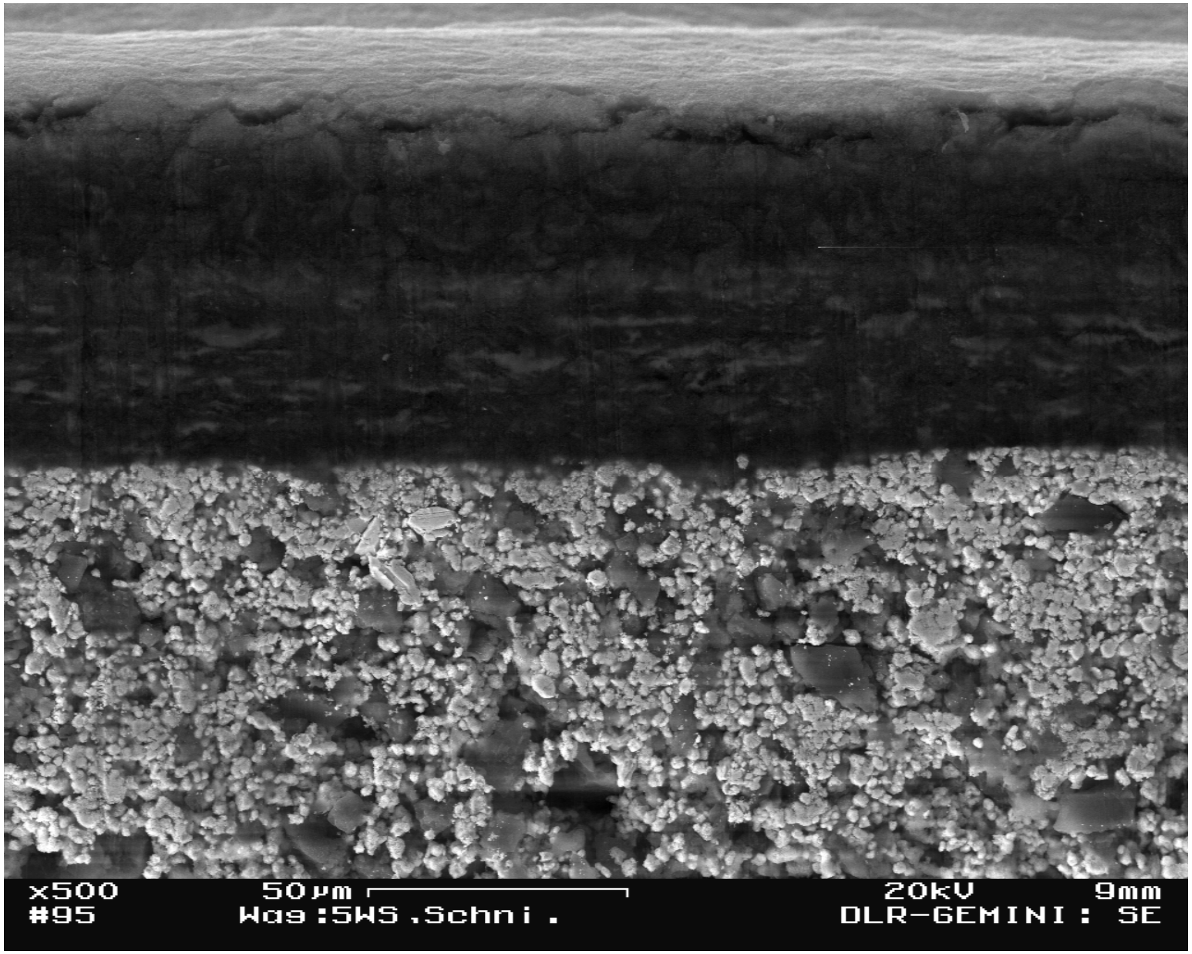
5 µm Pore radius



0,2 µm Pore radius

Multi-layer Gas Diffusion Electrodes

with different porous layers

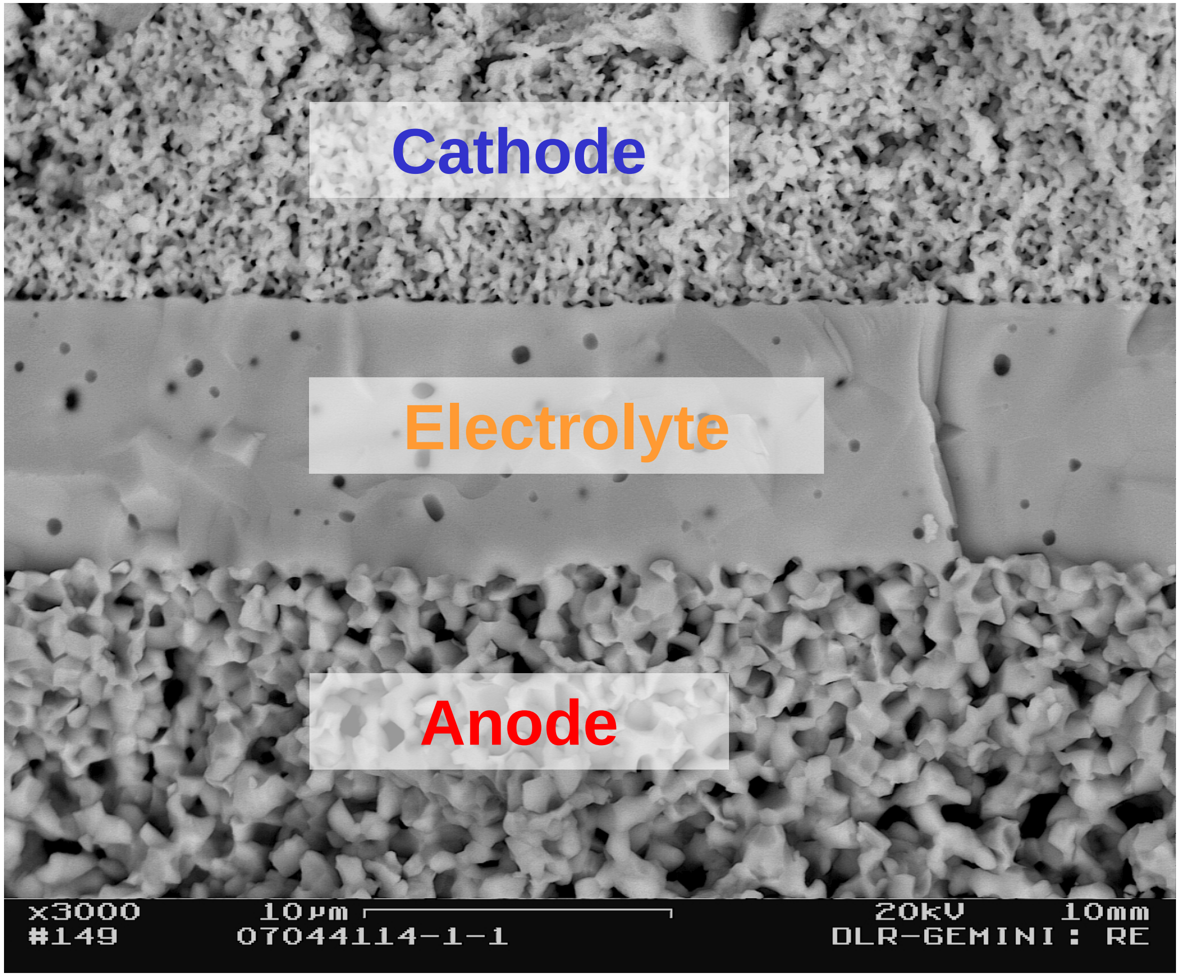


Dry sprayed C/PTFE

Reactive Mixing and Rolling Ag-PTFE

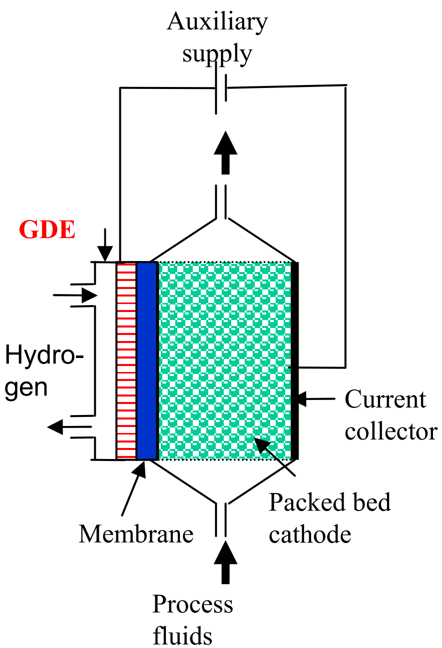
N. Wagner, T. Kaz, DE 101 12 232 A1, 2002

SEM micrograph of a cross section of SOFC



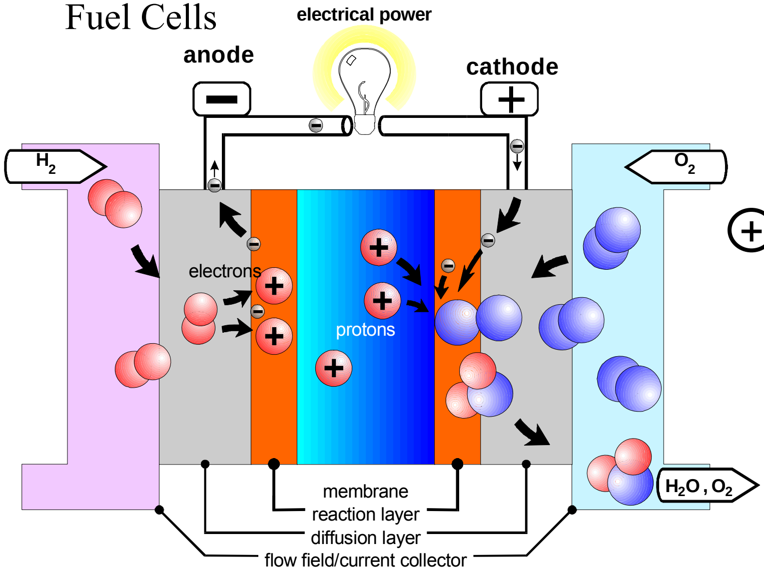
Field of application of porous electrodes

Water purification and treatment
(Bio)-Organic synthesis

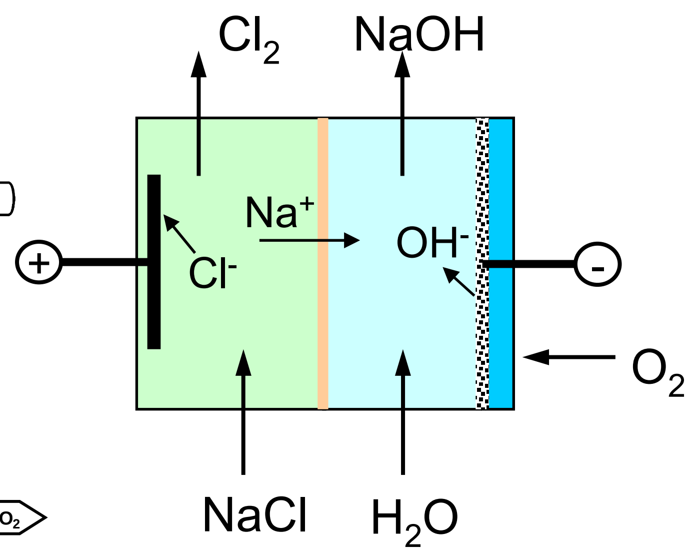


Batteries and supercaps

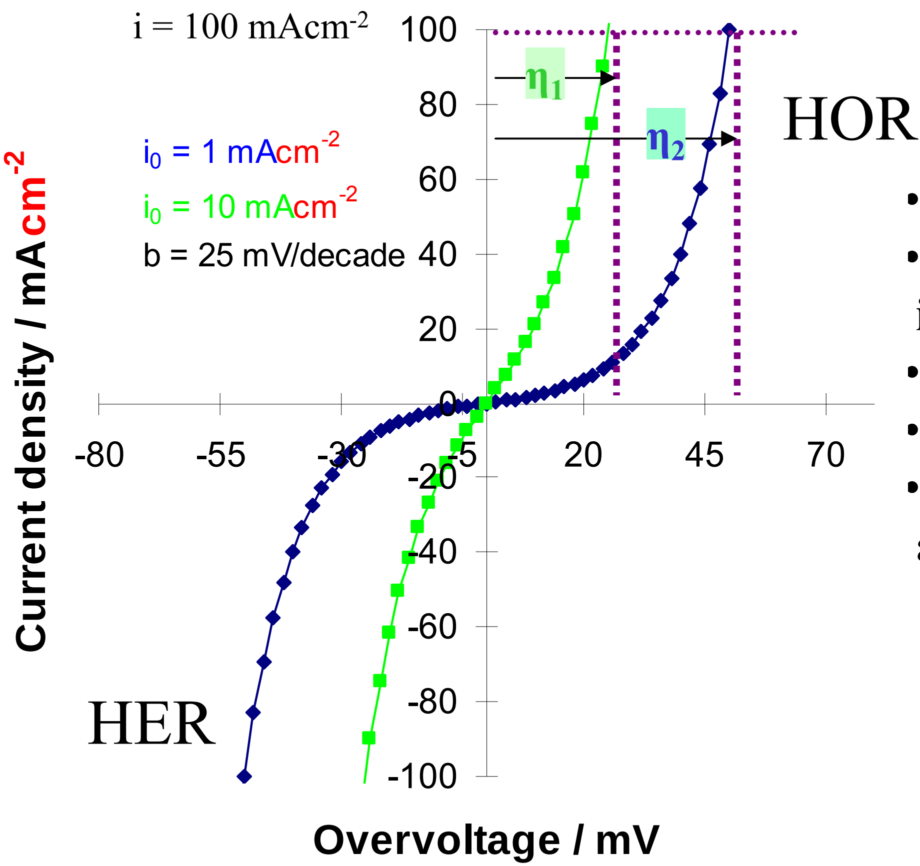
Fuel Cells



Electrolysis (Water, **NaCl**, HCl, etc.)



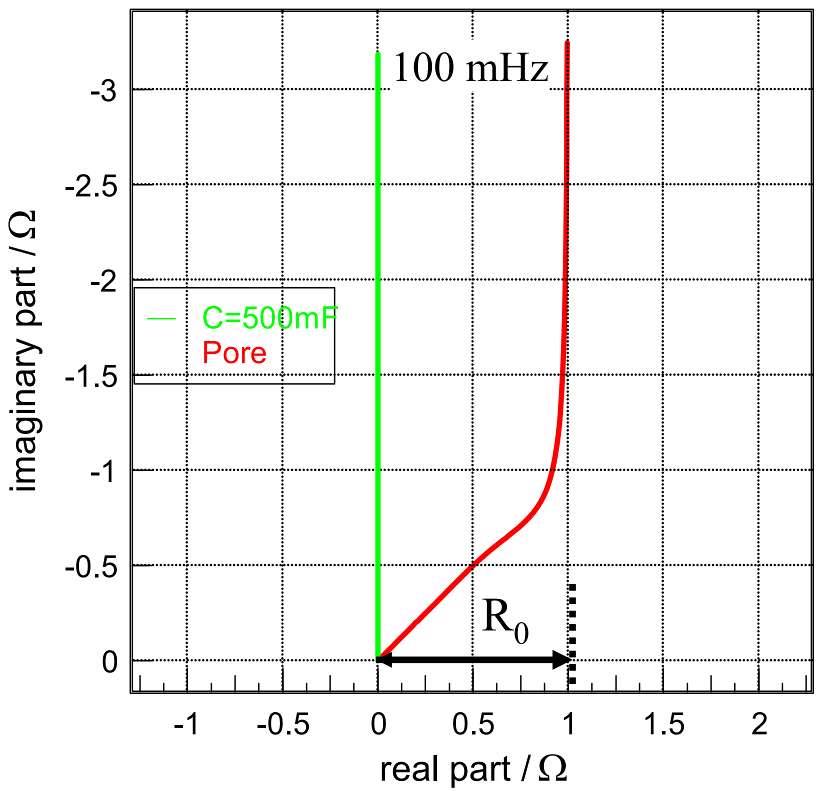
Why porous electrodes?

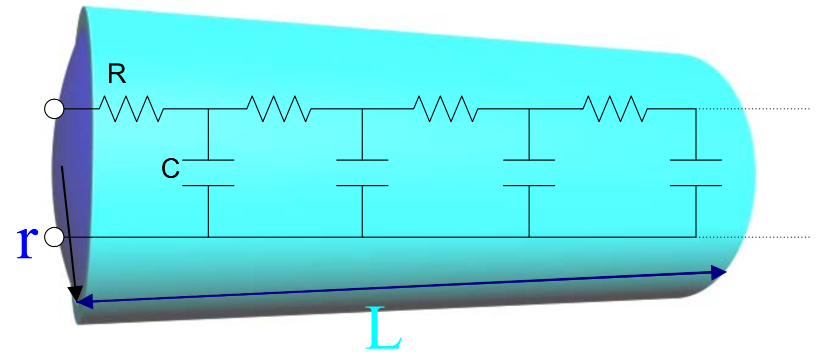


Butler-Volmer equation for hydrogen oxydation (HOR) and hydrogen evolution reaction (HER)

- **Enlargement of active electrode surface**
- **Lowering of overvoltage at same current input (electrolyzer) or output (fuel cell)**
- **Increasing of power density (galvanic cells)**
- **Increasing of storage capacity (supercaps)**
- **Lowering catalyst loading by increasing active surface**

Nyquist representation of Impedance of RC-transmission line, model of a flooded pore





R = 3 Ω

C = 0.5 F

$$Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC}$$

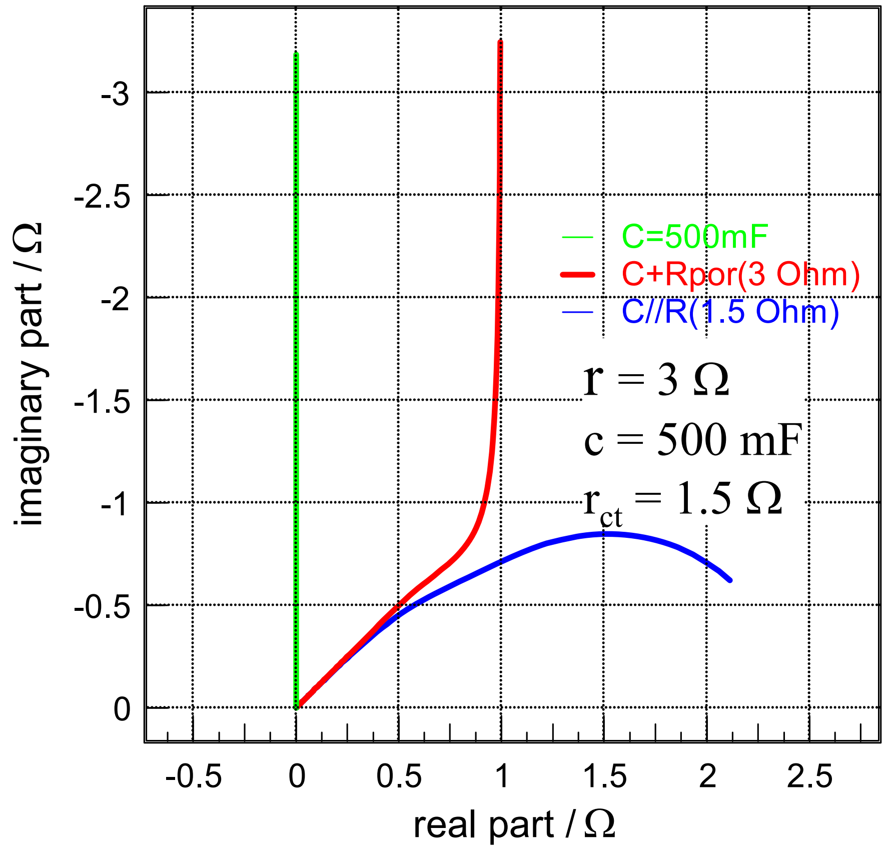
$$R_0 = R/3 = \delta L/3\pi r^2$$

δ = specific electrolyte resistance

r = pore radius

L = pore lenght

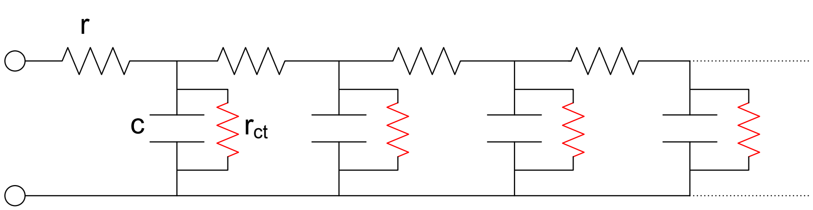
Nyquist representation of porous electrode impedance *with* faradaic impedance element



Simple pore model with faradaic processes in pores

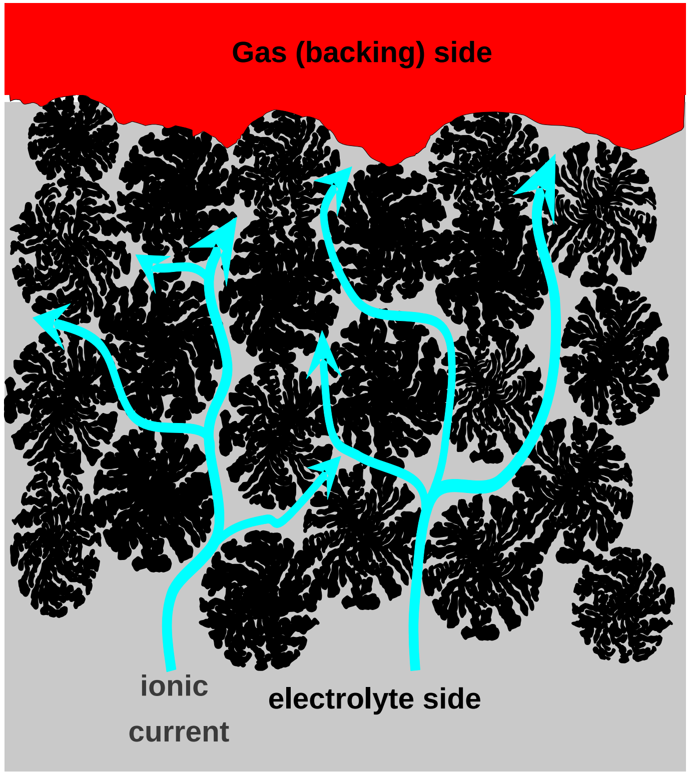
RC-transmission line of a flooded pore

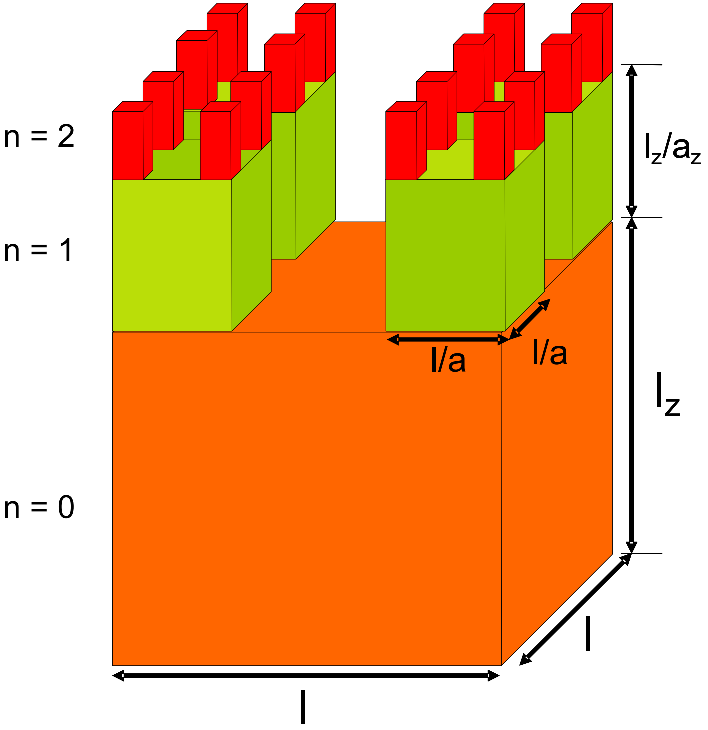
R. De Levie, Electrochim. Acta, **8**(1963) 751



Agglomerated Electrodes

Hierarchical model (Cantor-block model)

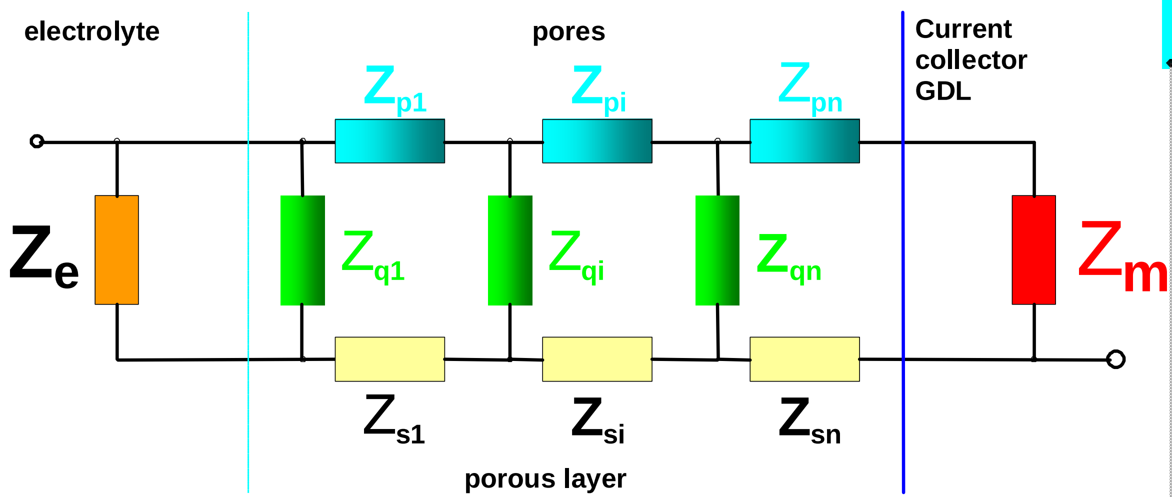


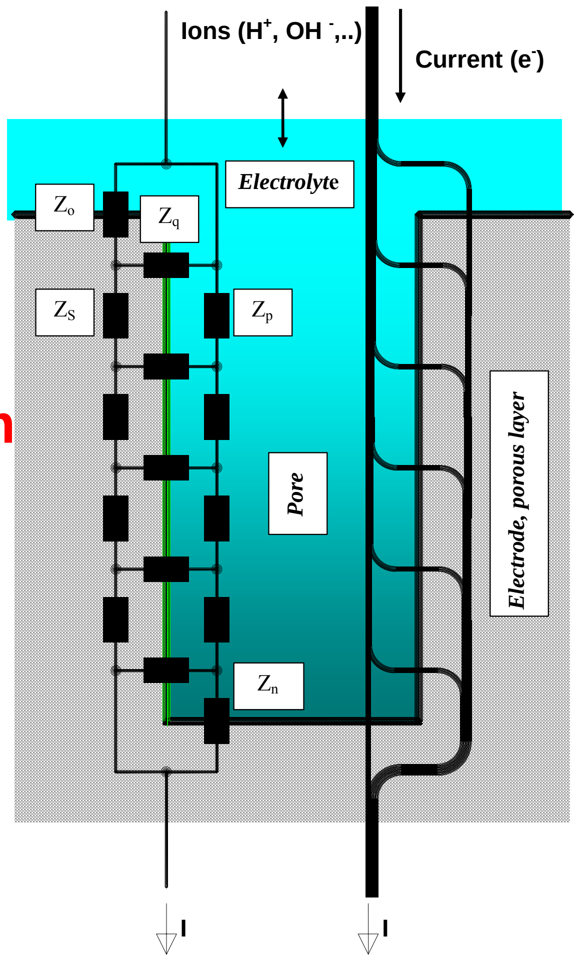


M. Eikerling, A.A. Kornyshev, E. Lust
J. Electrochem. Soc., **152** (2005) E24

S.H. Liu, *Phys. Rev. Letters*, **55**(1985) 5289
T.Kaplan, L.J.Gray, and S.H.Liu, *Phys. Rev.* **B 35** (1987) 5379

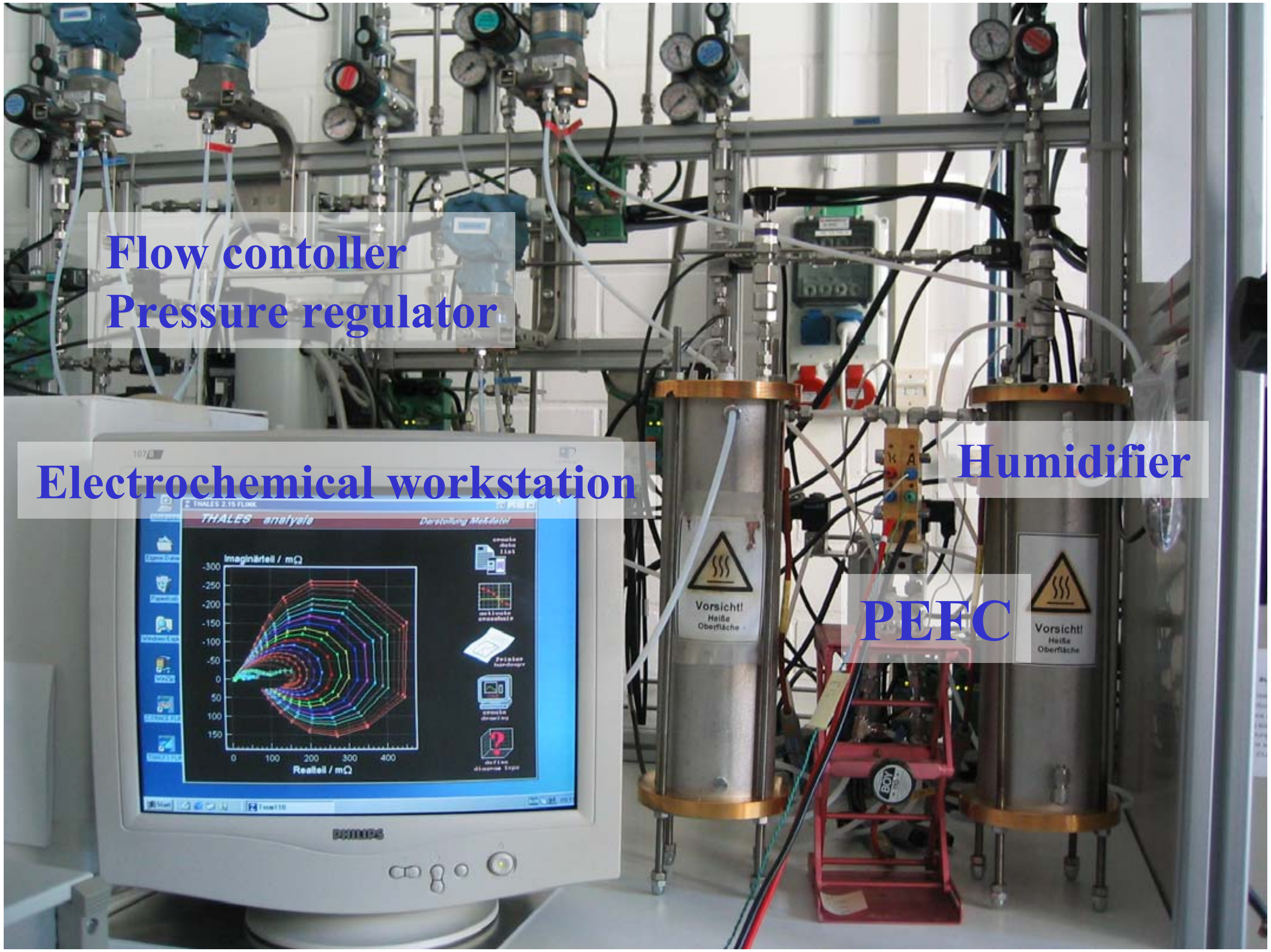
Cylindrical homogeneous porous electrode model (H. Göhr)



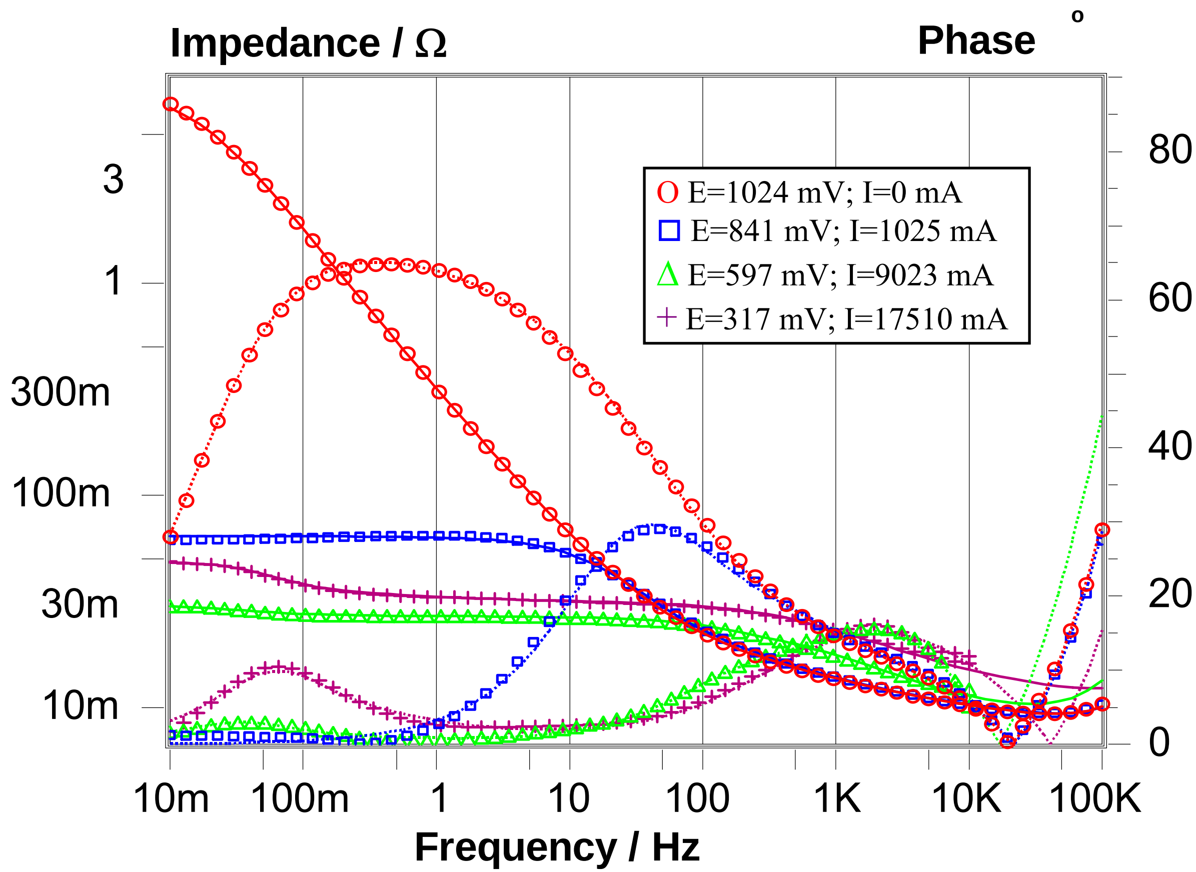


H. Göhr in *Electrochemical Applications/97*, www.zahner.de

Electrochemical Impedance Spectroscopy: Experimental Set-up

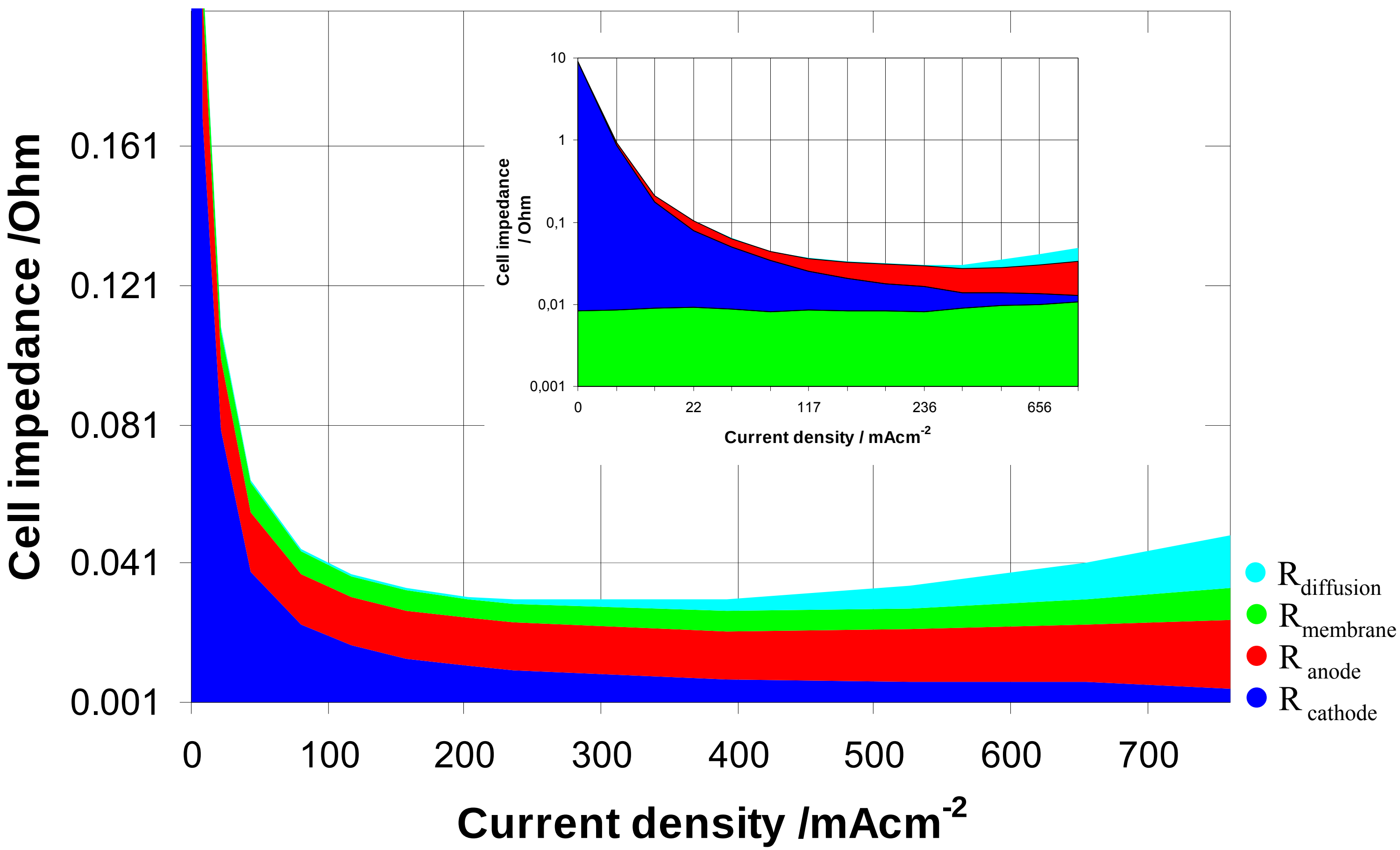


Bode diagram of measured EIS at different cell voltages

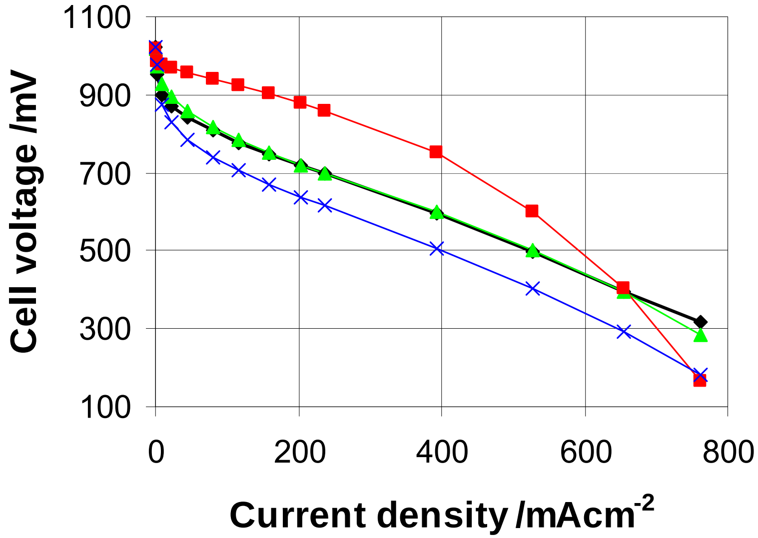


EIS at Polymer Fuel Cells (PEFC):

Contributions to the cell impedance at different current densities



Evaluation of the U-i characteristics from EIS



◆ measured curve: $U_n = f(i_n)$

■ calculated curve: $U_n = i_n R_n$ (without integration)

Δ calculated curve using method II: $U_n = a_n i^2_n + b_n i_n + c_n$

x calculated curve using method I: $U_n = a_n i_n + b_n$

$$R_n = \frac{\partial U}{\partial I}\Big|_n$$

Integration method I:

$$U_n = U_{n-1} - \tfrac{1}{2}\left(\frac{\partial U}{\partial I}\Big|_{n-1} + \frac{\partial U}{\partial I}\Big|_n\right) * (I_n - I_{n-1})$$

Integration method II:

$$U_n = a_n I_n^2 + b_n I_n + c_n \quad \text{with:}$$

$$a_n = \frac{R_{n+1} - R_n}{2(I_{n+1} - I_n)}$$

$$b_n = R_{n+1} - 2a_n I_{n+1}$$

$$c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1}$$

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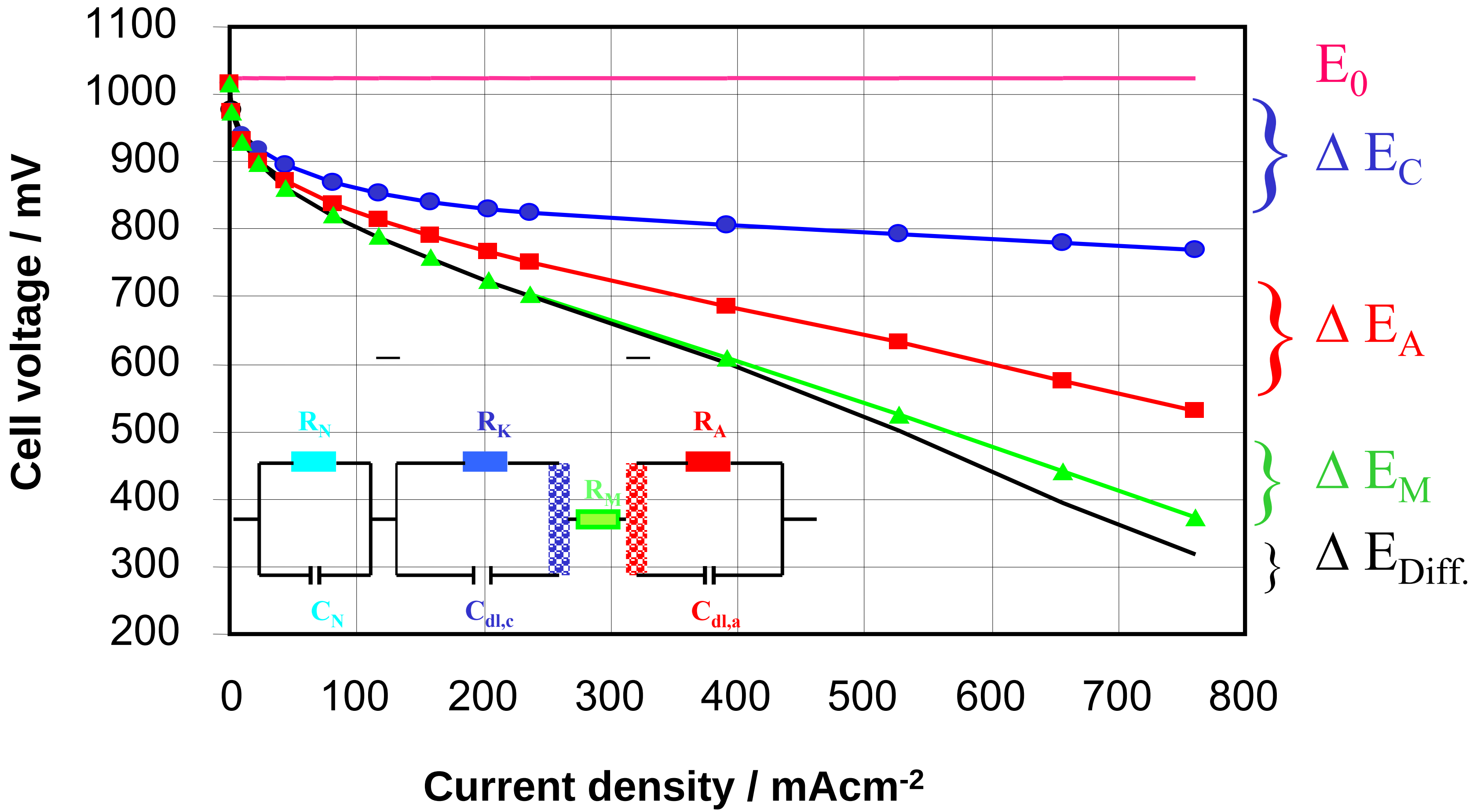
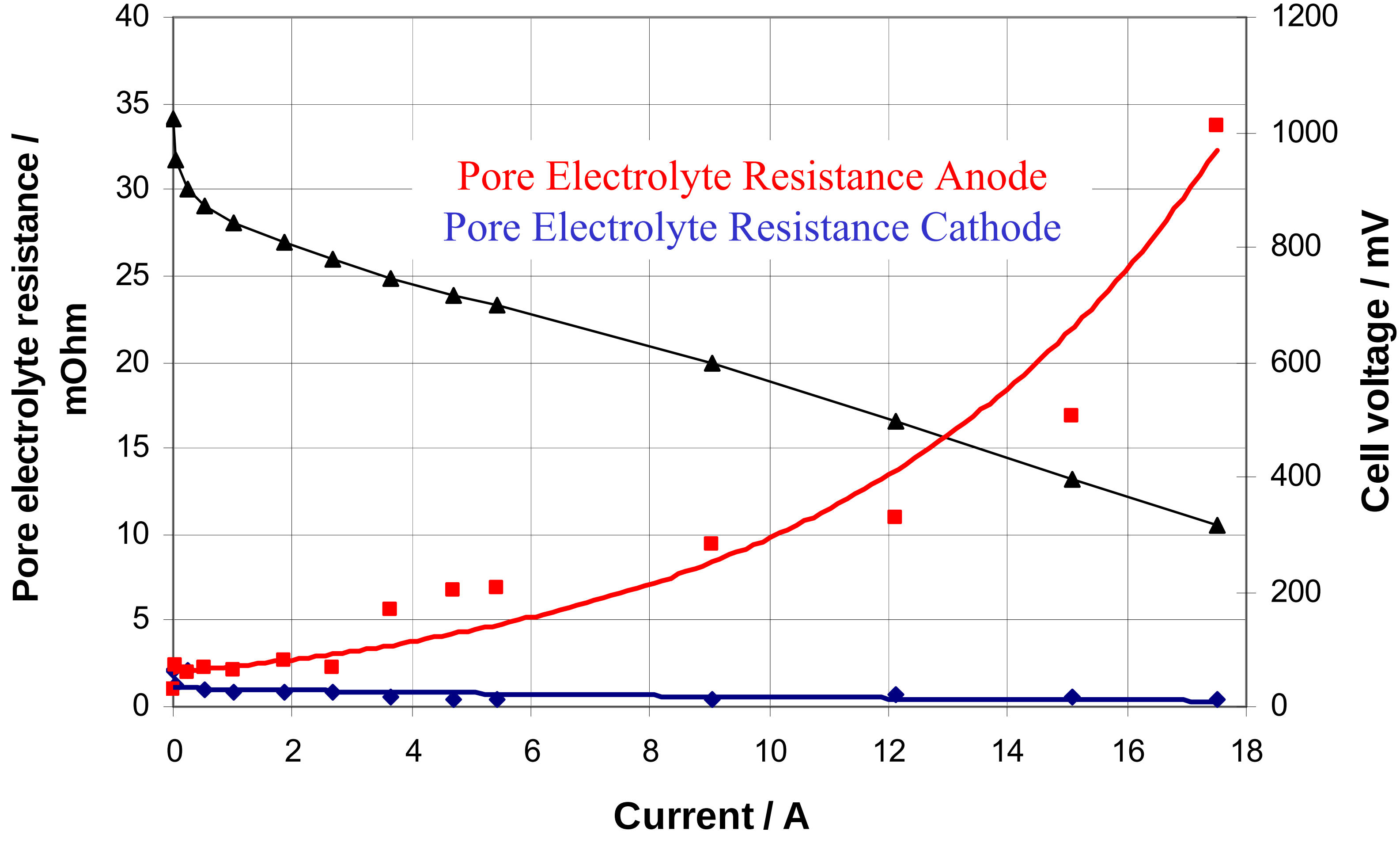
EIS at Polymer Fuel Cells (PEFC):

Contributions to the overal U-i characteristic determined by EIS

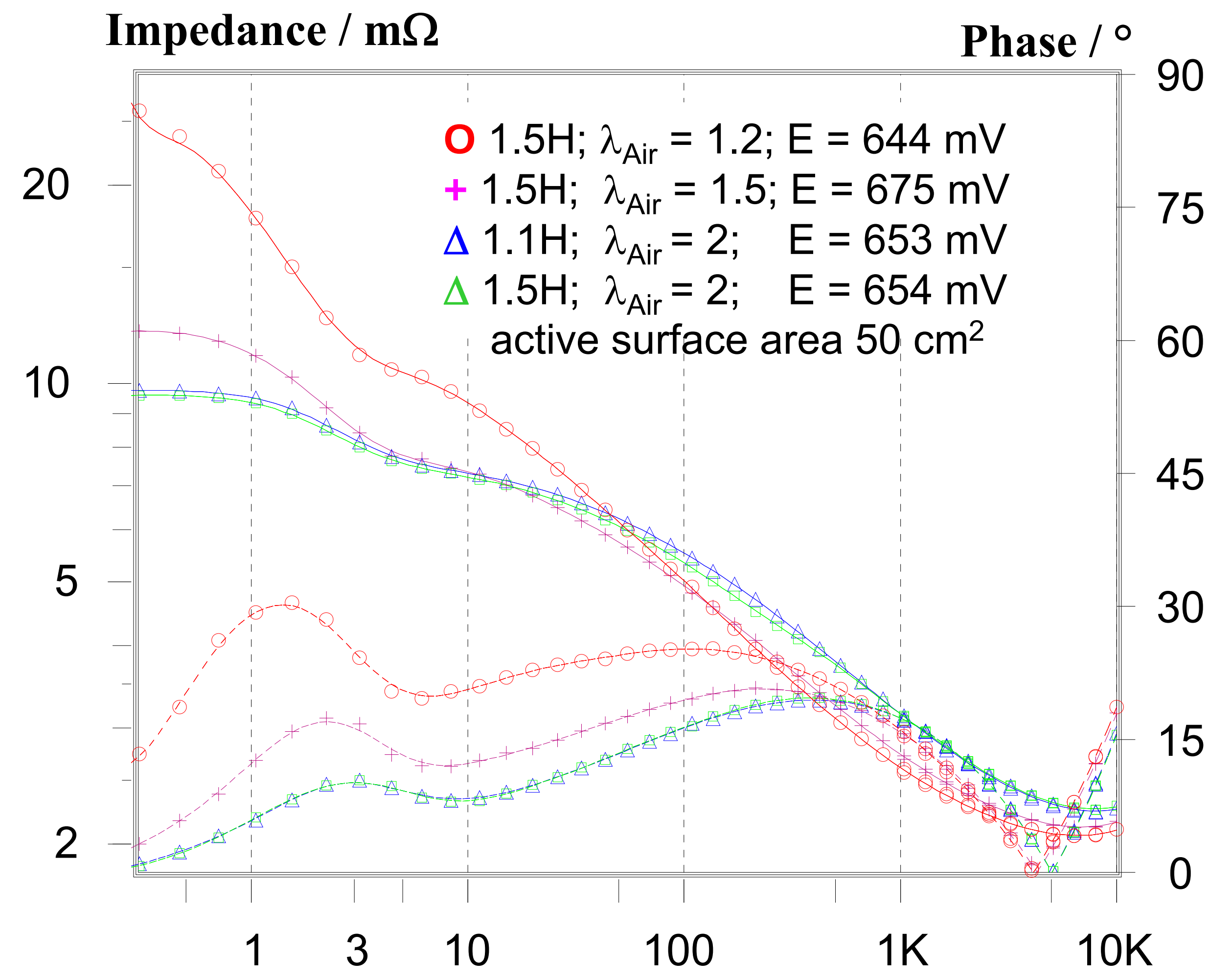


Evaluation of EIS with the porous electrode model

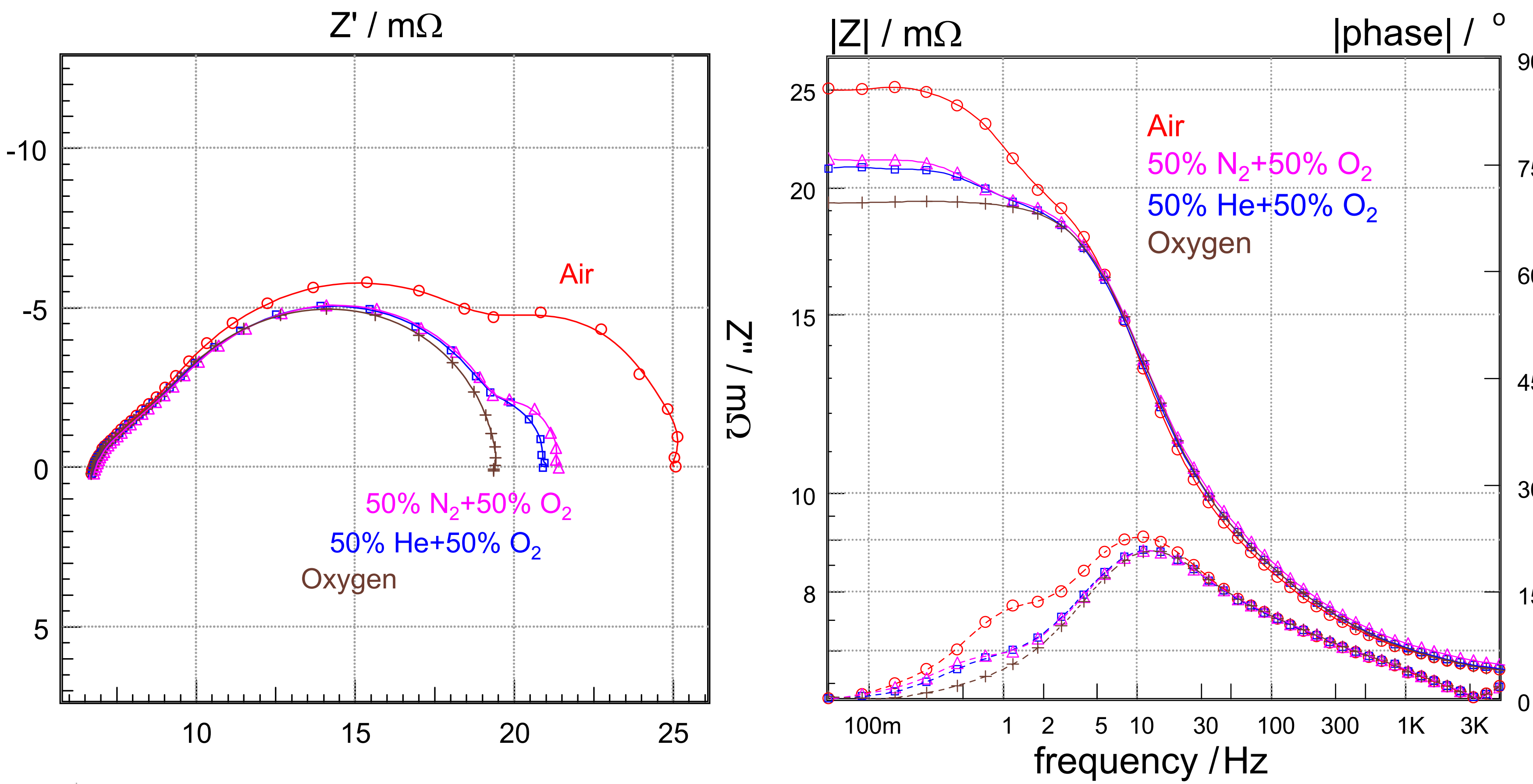
Summary of current density dependency of pore resistance elements



Bode Diagram of EIS, measured at PEFC, 75°C, 0.5 Acm^{-2}
Variation of gas flow rates

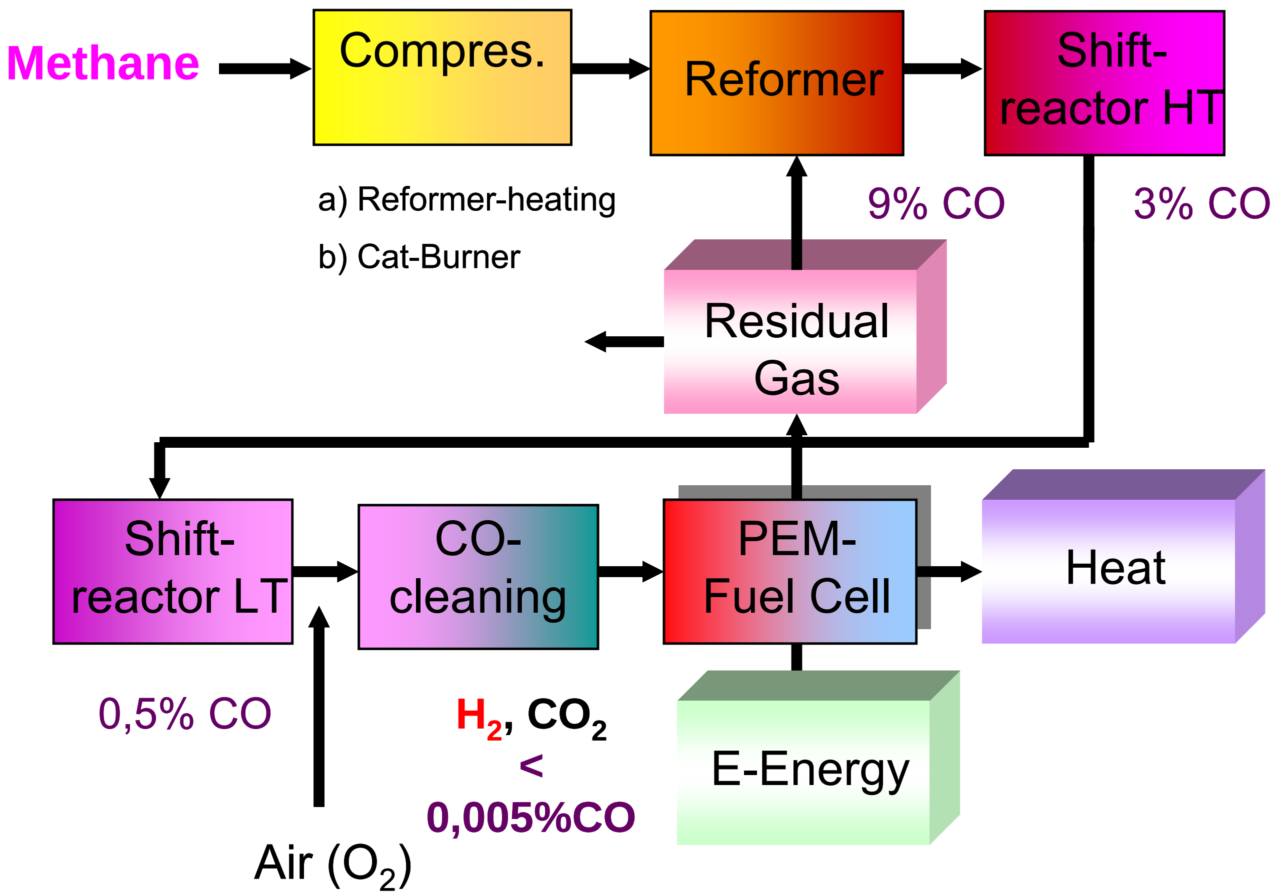


Comparison of EIS measured at 5 A, 80°C, λ=1.5, cathode fed with different gas composition

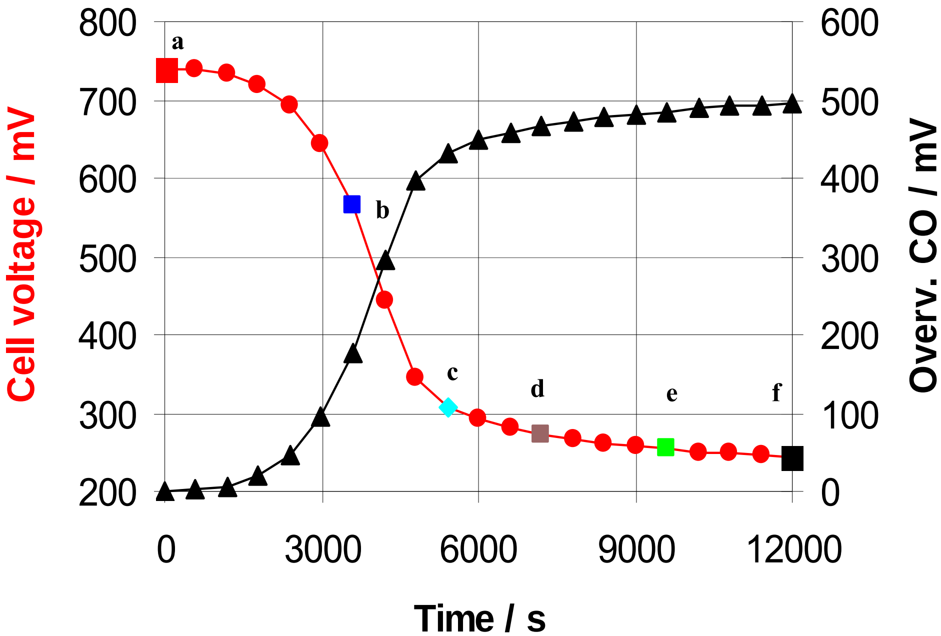


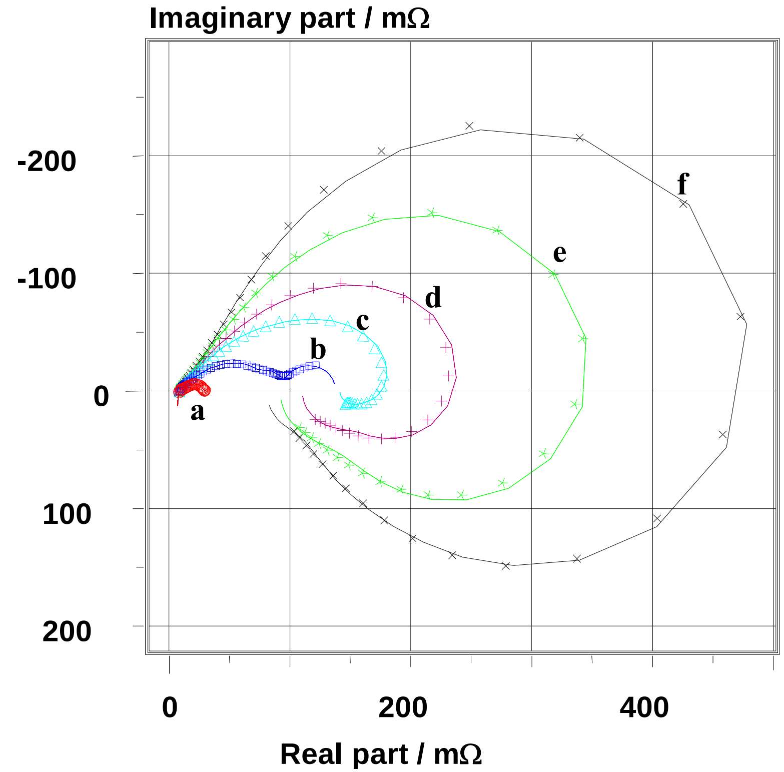
Reforming of Methane

$$CH_4 + 2H_2O \Rightarrow 4H_2 + CO_2\ (CO)$$



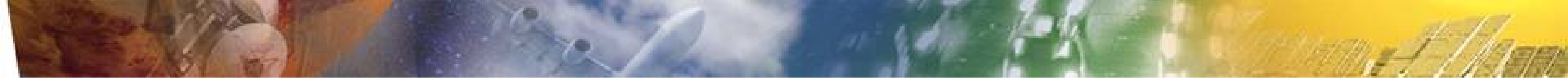
Time resolved EIS - CO poisoning of Pt-anode



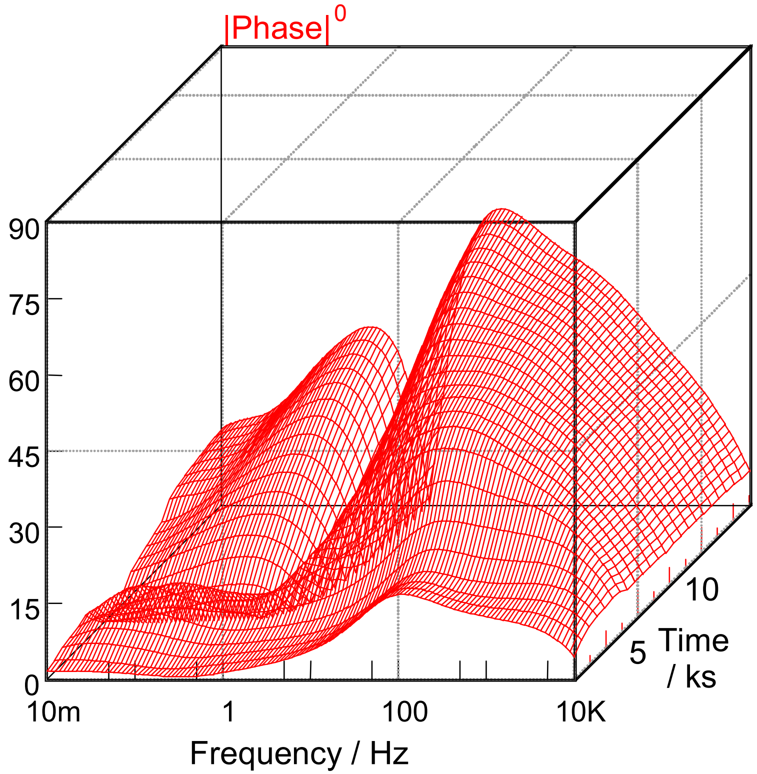


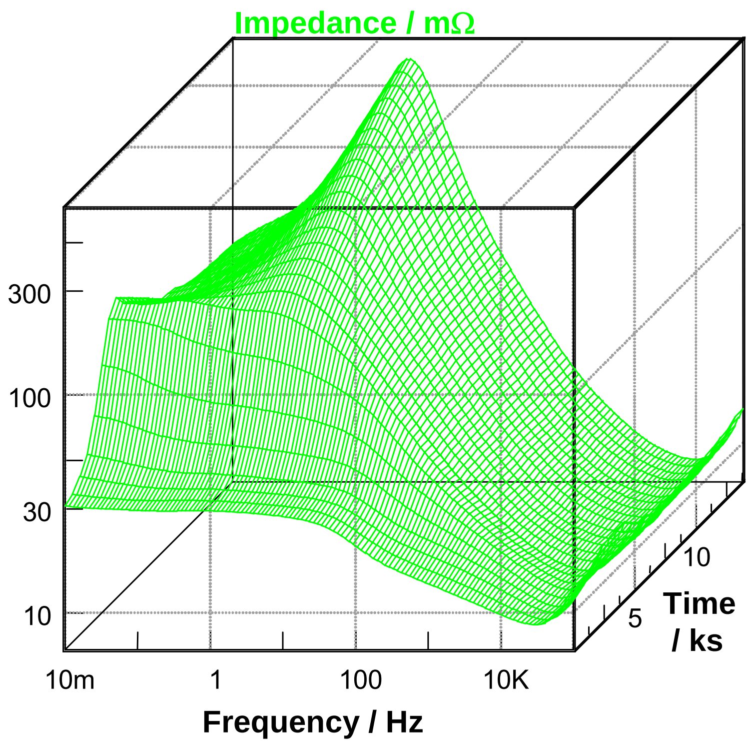
Time progression of **cell voltage** and overvoltage in galvanostatic mode of PEFC operation (217 $mAcm^{-2}$) Pt-anode , H_2 + 100 ppm CO at 80°C

Nyquist plot of **EIS** measured at different times during poisoning of the Pt-anode with CO



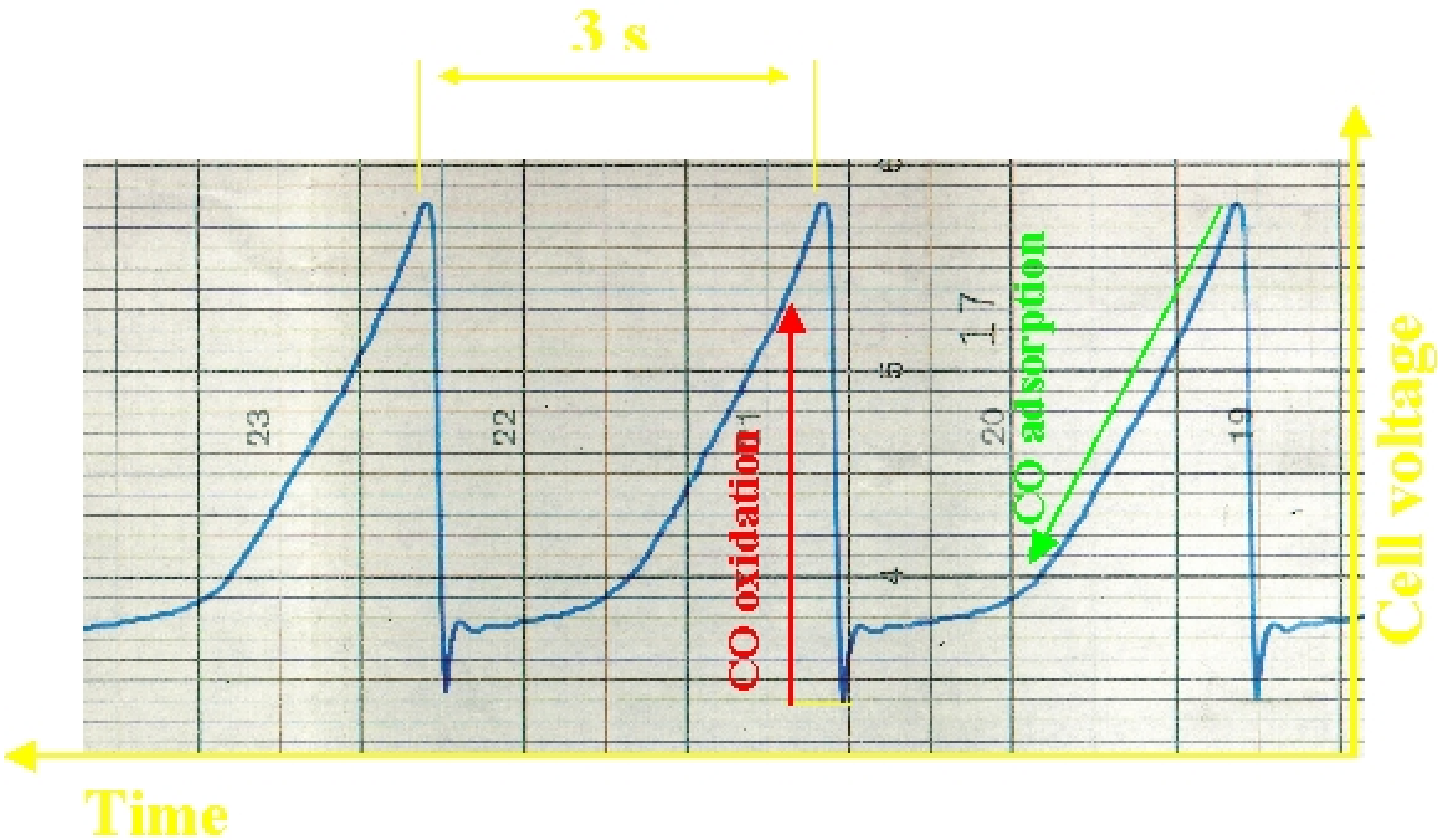
Time resolved EIS - CO poisoning



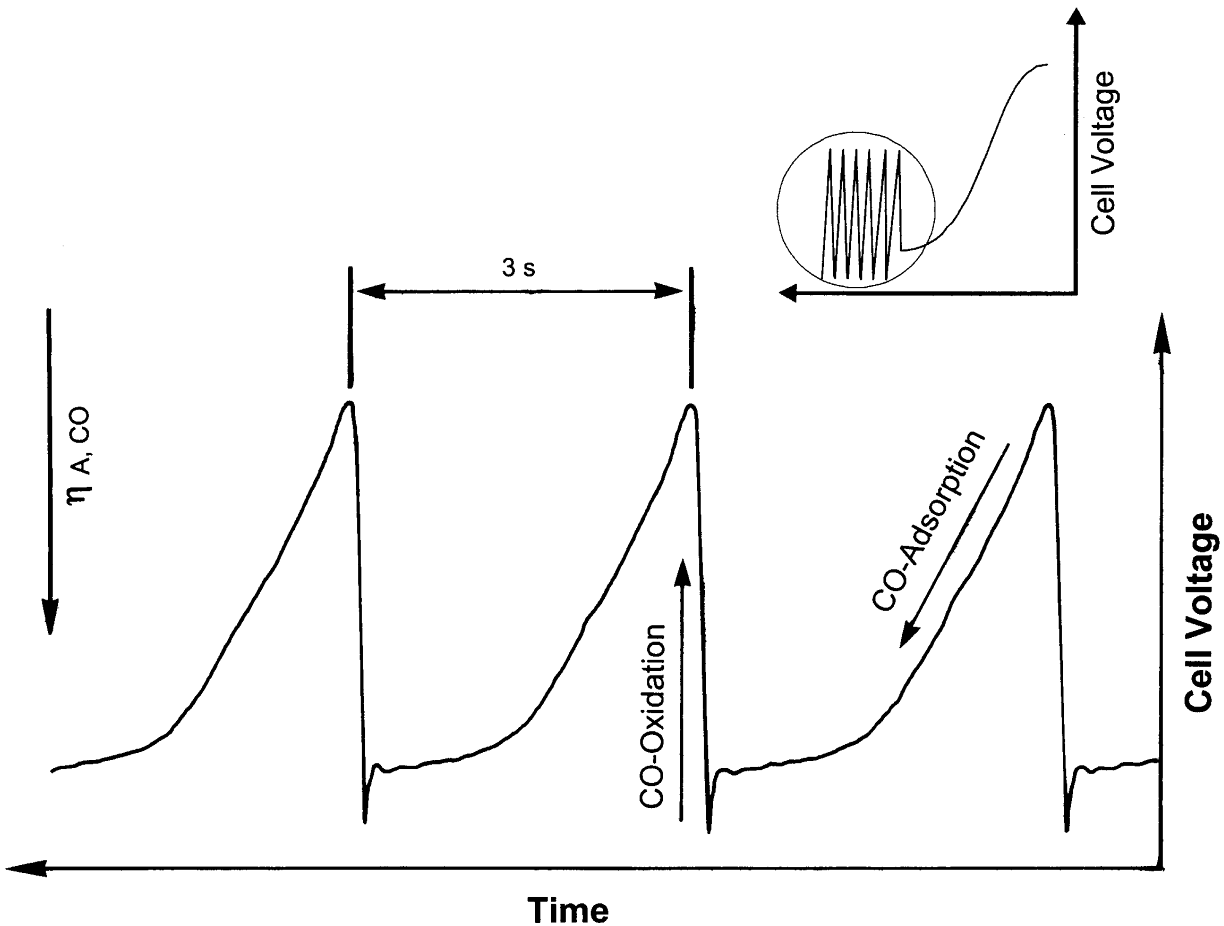


Bode plot of EIS during CO poisoning of the Pt-anode at 217 mAcm^2, H_2+100 ppm CO

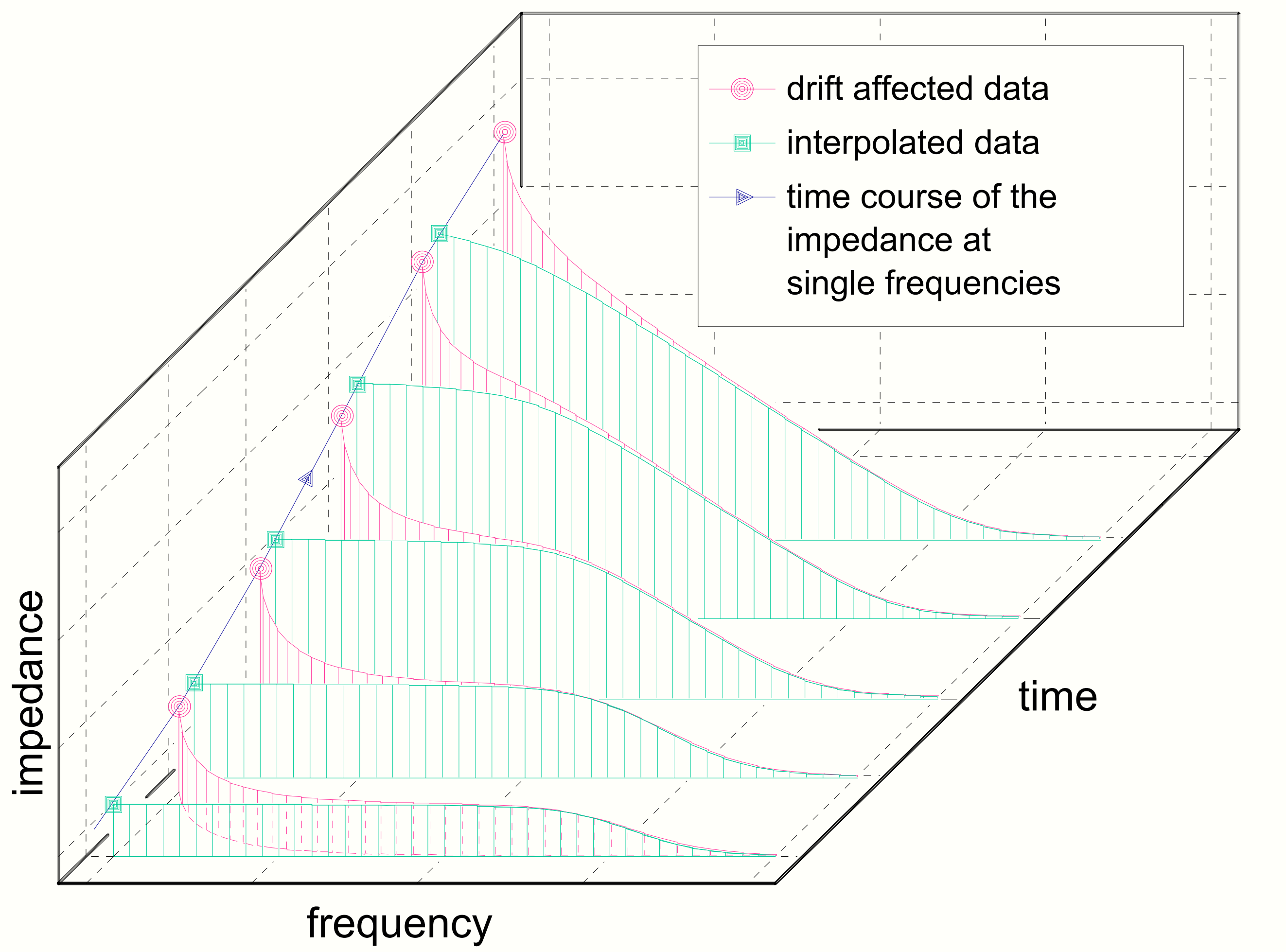
Appearance of voltage oscillations during galvanostatic operation of PEFC with H_2+CO



Appearance of voltage oscillations during galvanostatic operation of PEFC with H_2+CO



Improved evaluation techniques
Time course interpolation

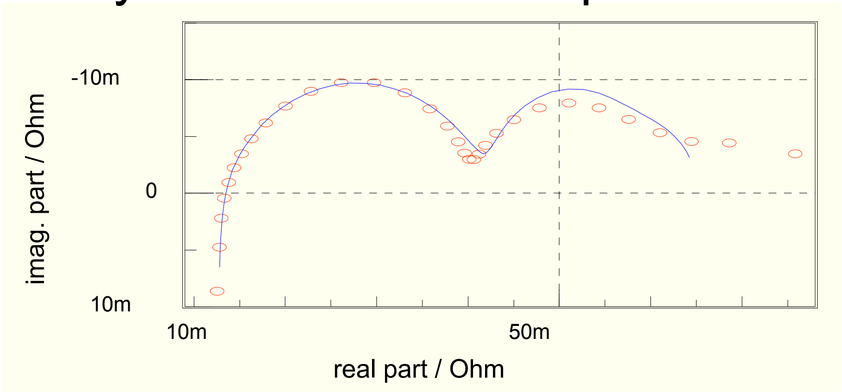


Requirements

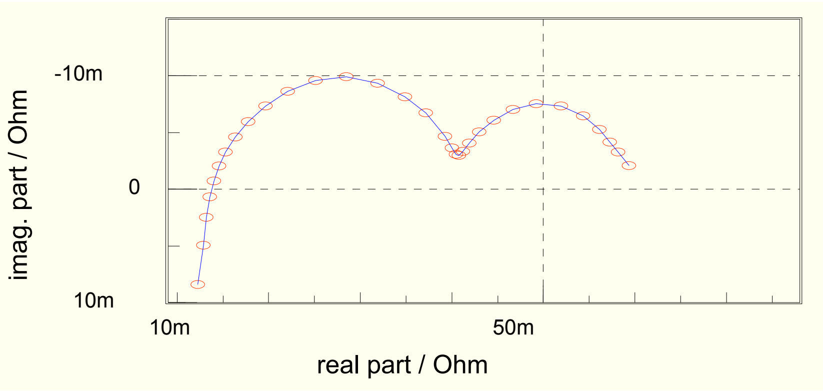
- Series measurement
- Time for each
- measured frequency AND for each spectrum

Results of the improved evaluation techniques

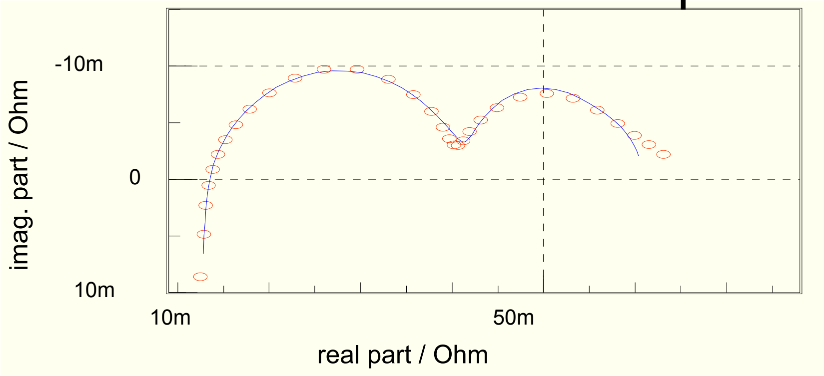
I. Only real-time drift compensation



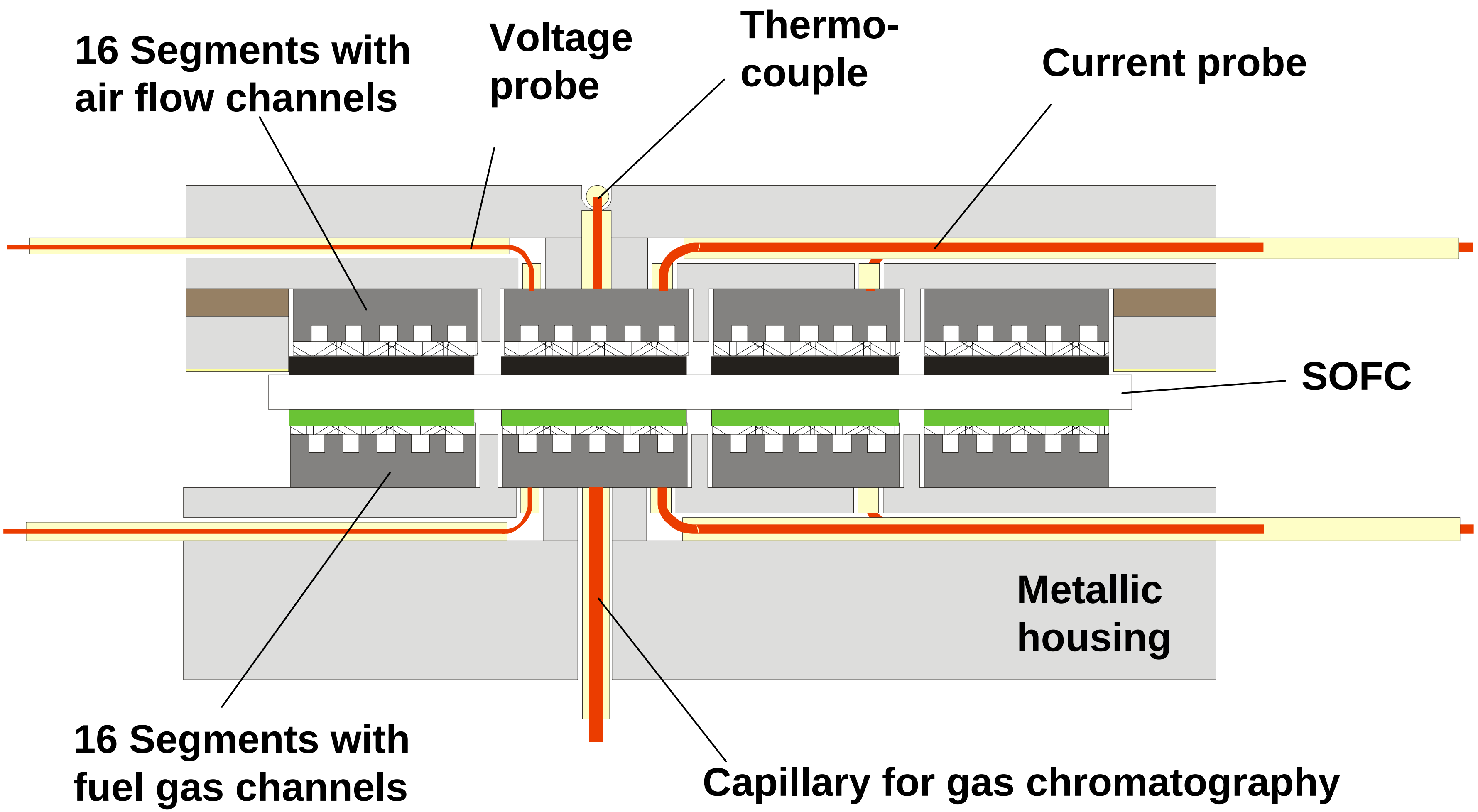
III. Z-HIT refinement

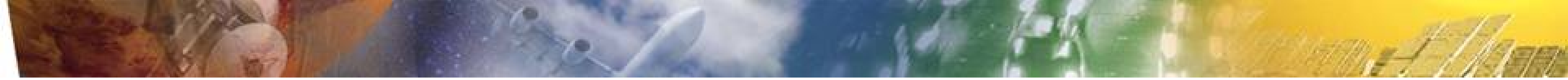


II. Additional time course interpolation

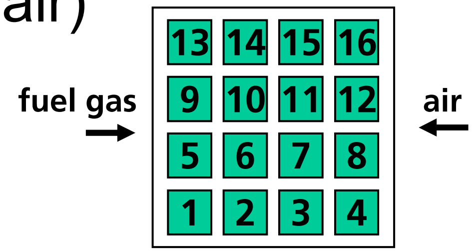


Segmented SOFC cell design with segmented bipolar plates

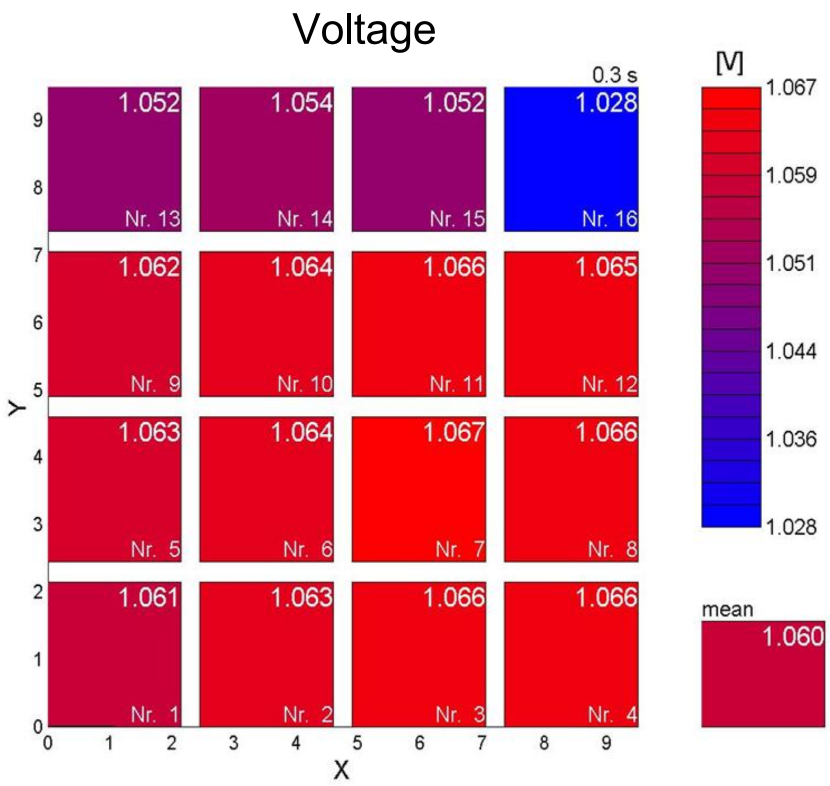




OCV distribution of ASC at 800°C and simulated reformate (50% H_2 + 50% N_2 + 3% H_2O, 0.08 SlpM/cm² air)



Fuel gas



Air

Nernst equation:

$$U_{rev} = U_{rev}^{0} - \frac{RT}{zF} \ln\left(\frac{p_{H2O}}{\sqrt{p_{O2}}\, p_{H2}} \right)$$

Produced water:

S4: 0.61%,

S8: 0.72%,

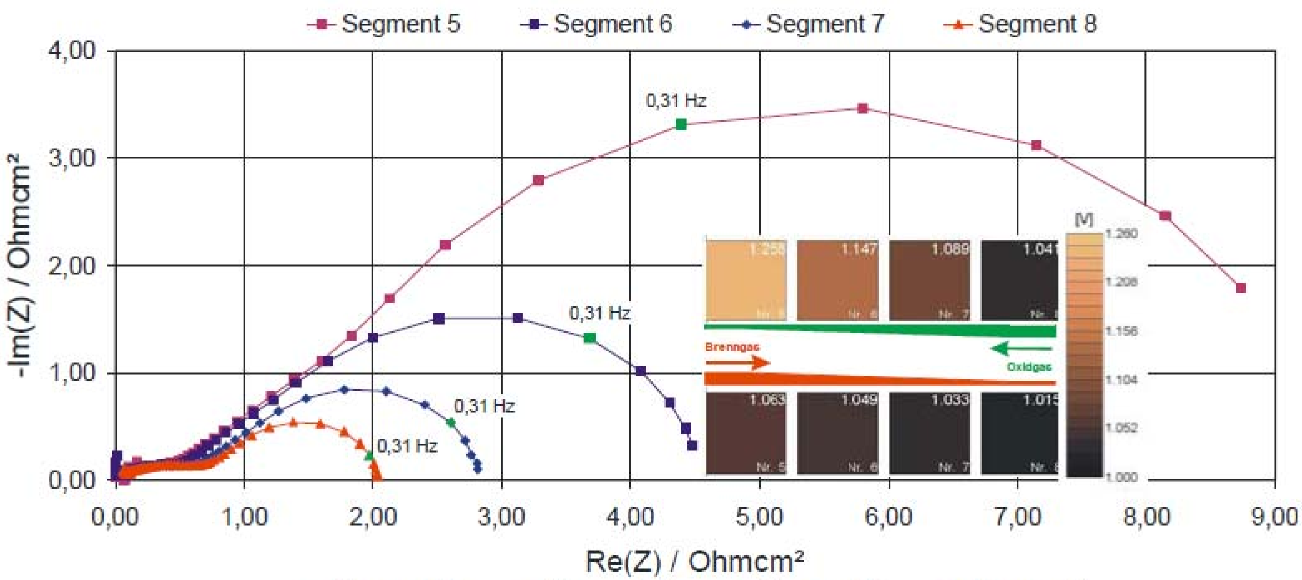
S12: 0.78%,

S16: 3.30%

EIS at OCV, ASC with segmented cathode, 77.44 cm²

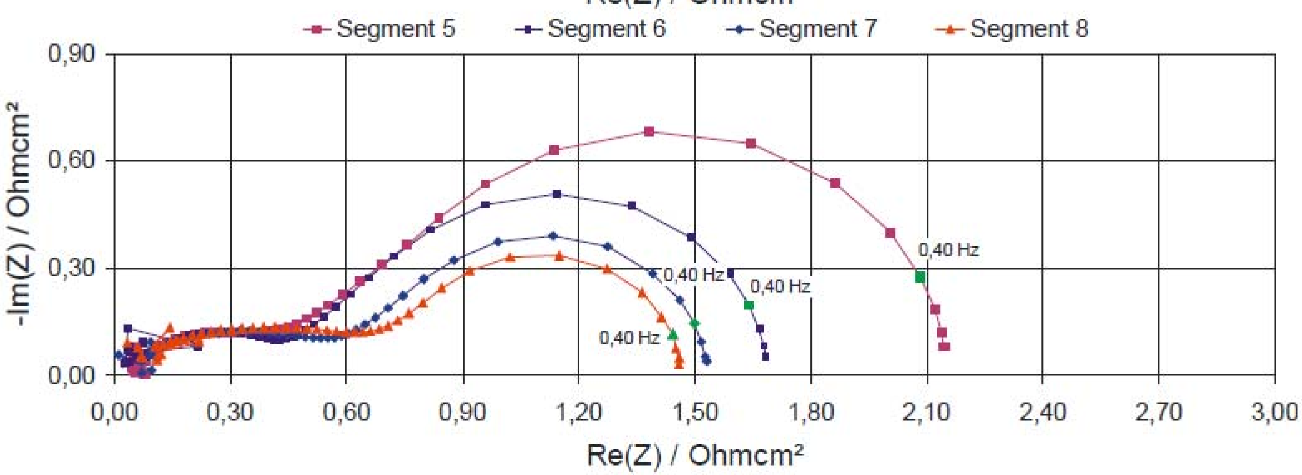
a)

Dry hydrogen



b)

Hydrogen+ 3% H_2O

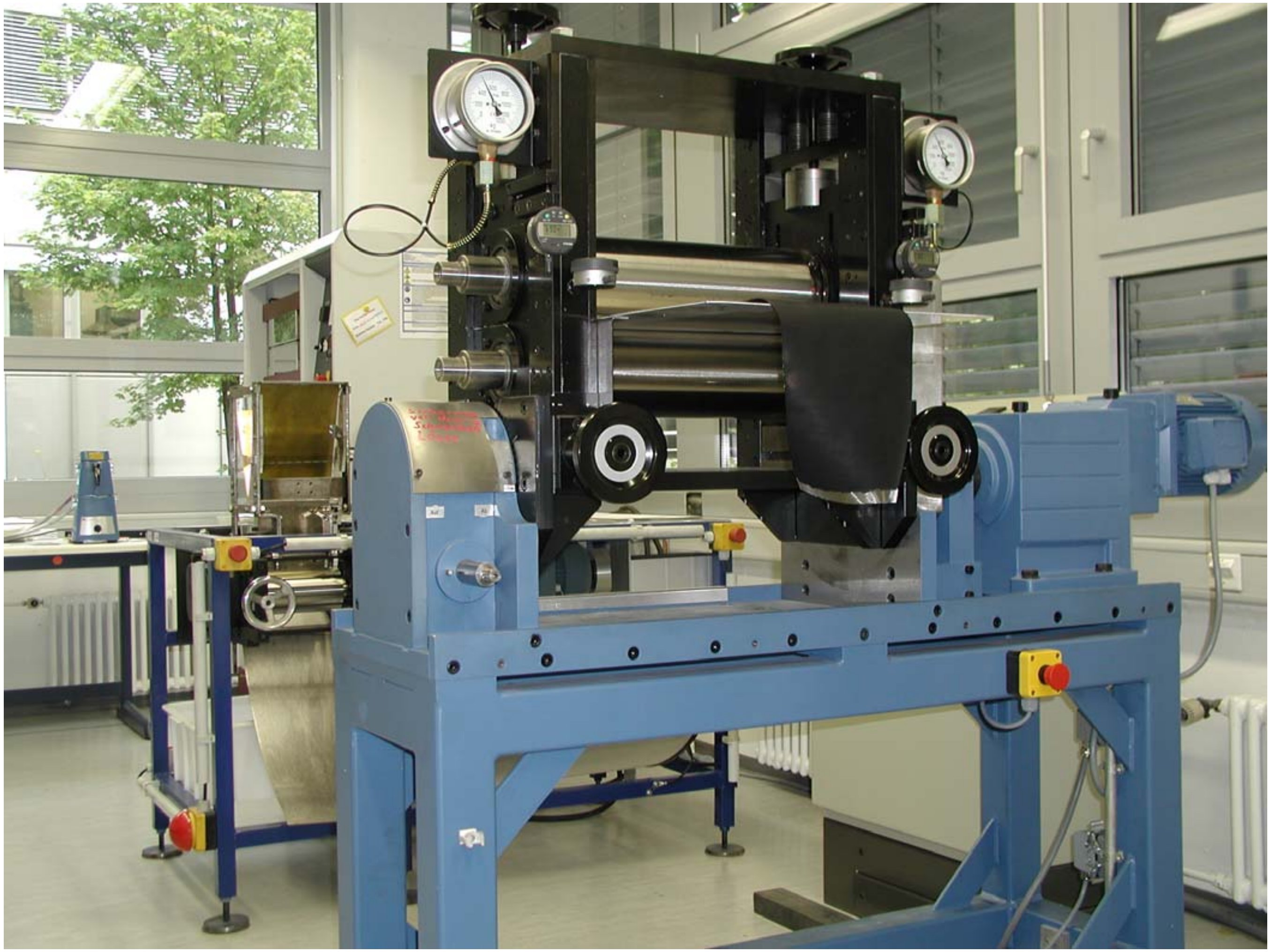


Oxygen Reduction in Alkaline Media

- Cathode of the alkaline fuel cell
- Cathode in metal-air batteries
- Cathode in the electrolyzer for chlorine production (ODC, Oxygen Depolarizing Cathode)

Reactive Mixing and Rolling (RMR)

GDE Production Technique for AFC Electrodes



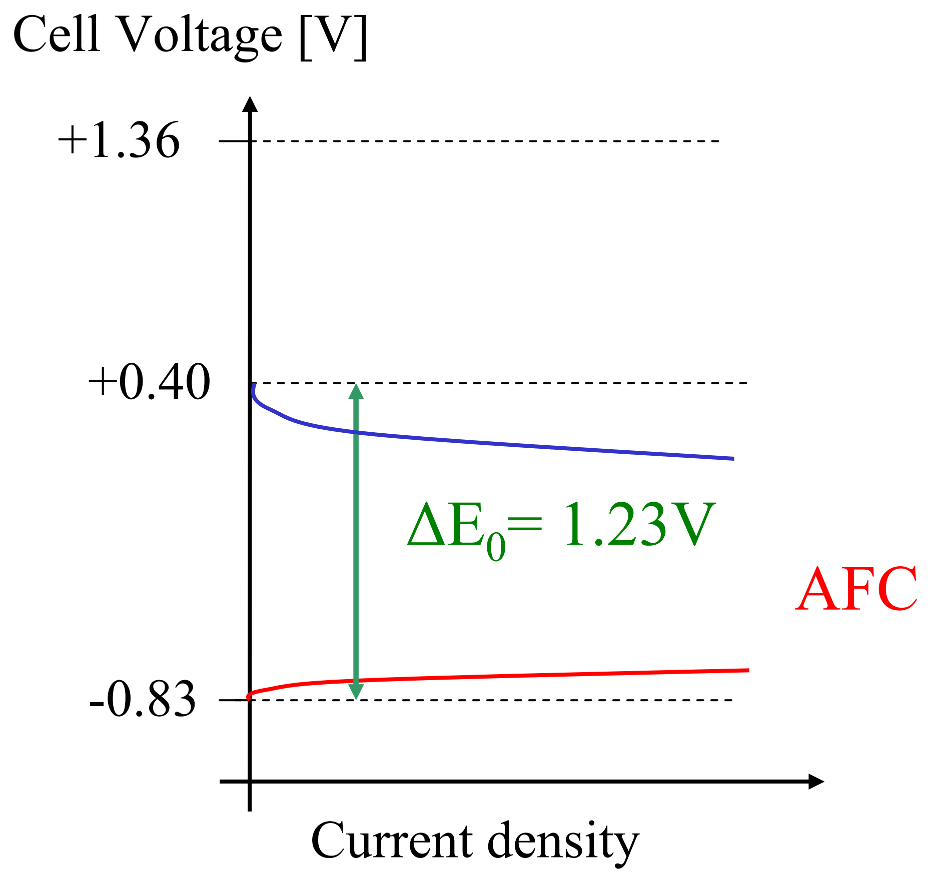
Schematically representation of cell voltage and potentials in an alkaline fuel cell

Cathode with ORR

$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Anode

$2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4\ e^-$



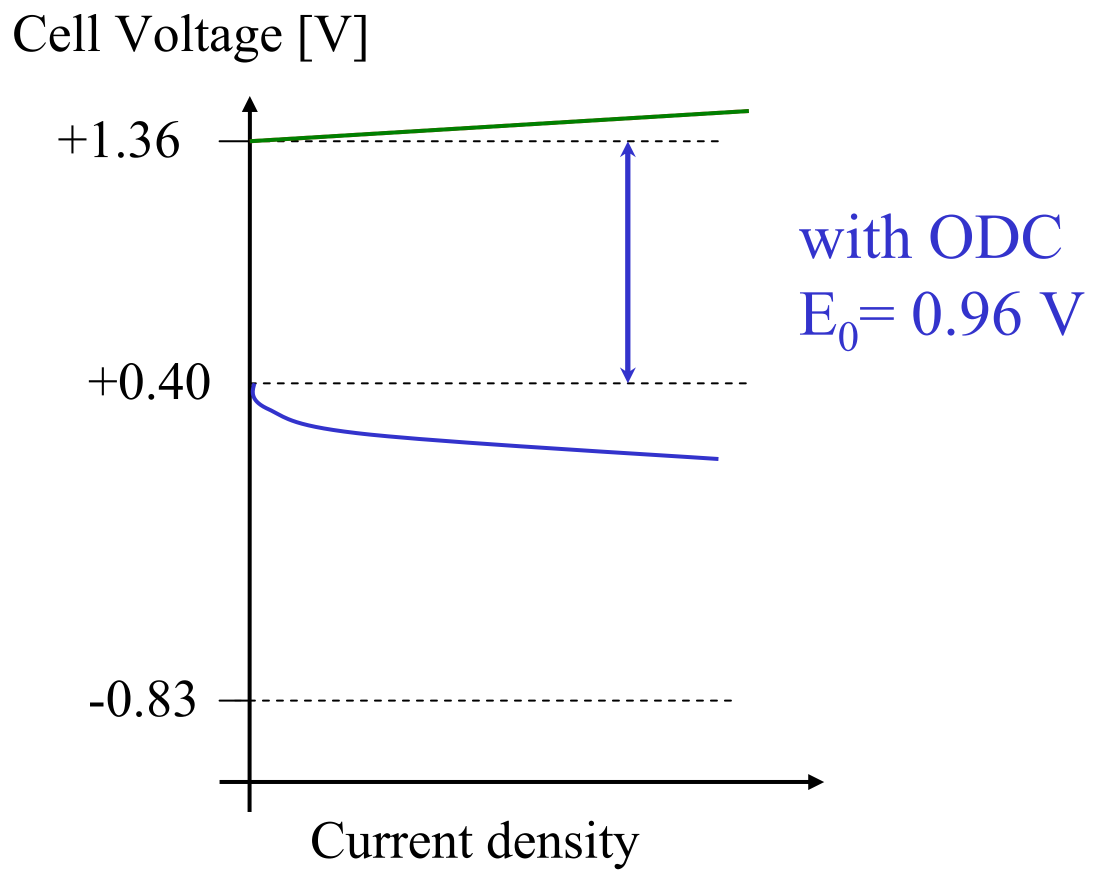
Cell voltage and potentials in an electrolyzer for chlorine production

Anode

$4\ Cl^- \rightarrow 2\ \mathbf{Cl_2} + 4\ e^-$

Cathode with ORR

$\mathbf{O_2} + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

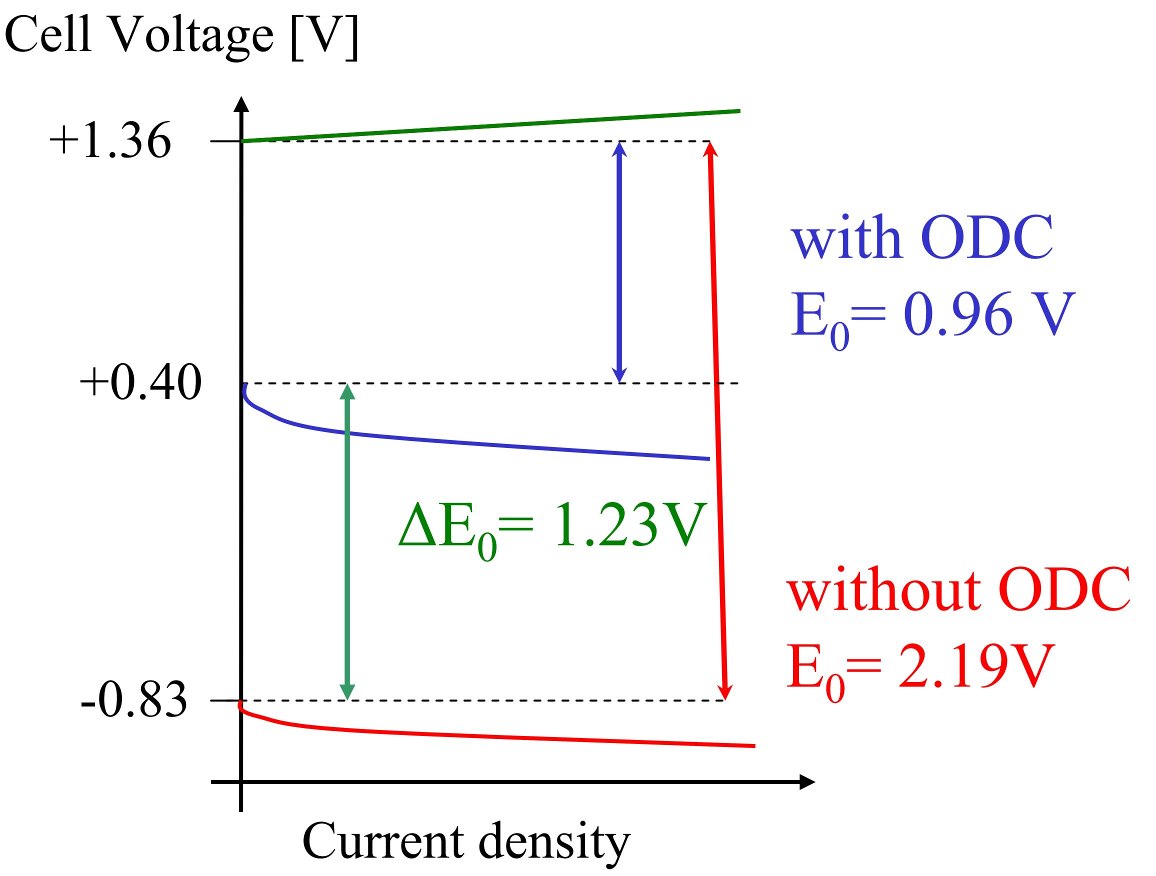


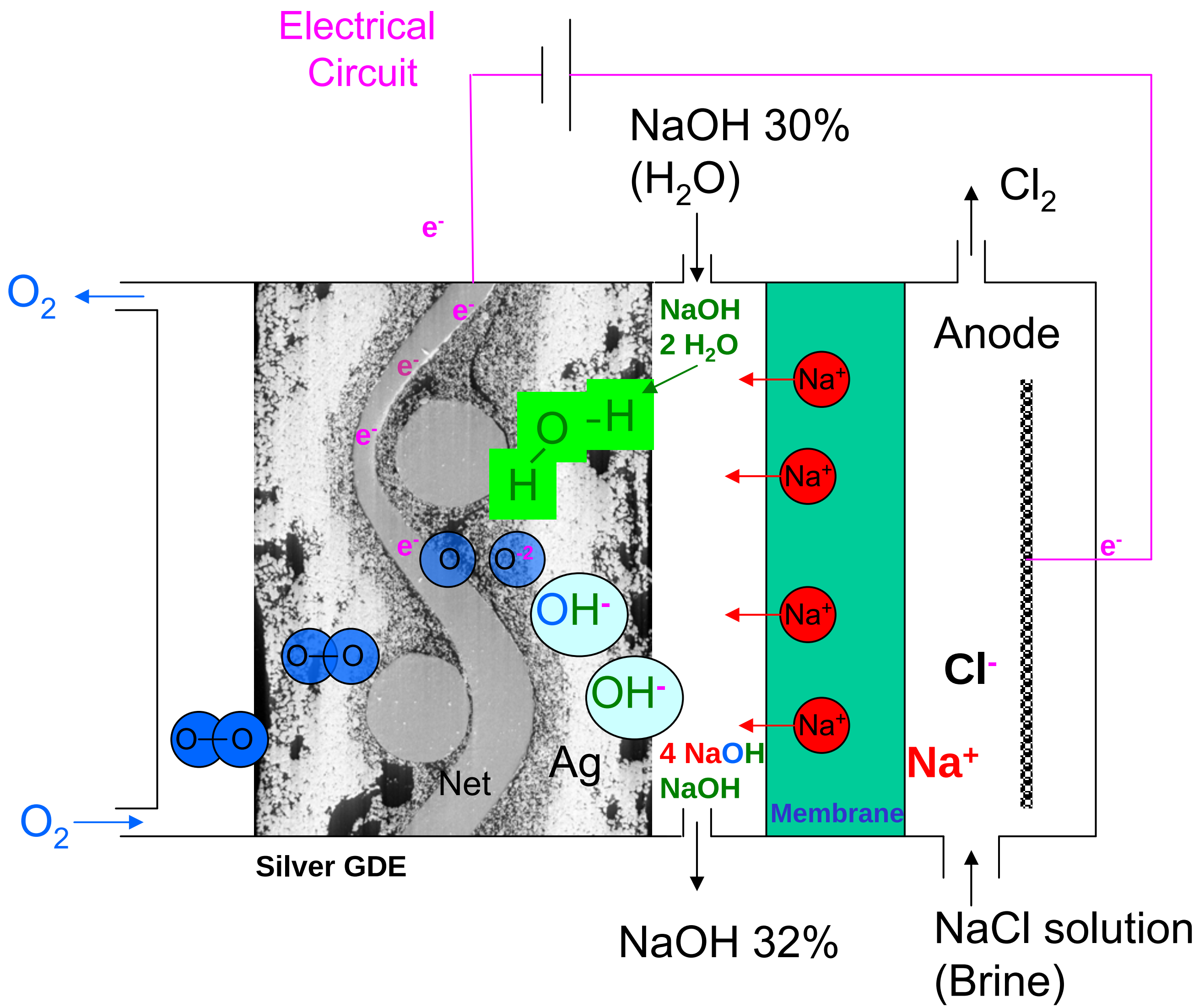
Cell voltage and potentials in an electrolyzer for chlorine production

Anode
$4\ Cl^- \rightarrow 2\ \mathbf{Cl_2} + 4\ e^-$

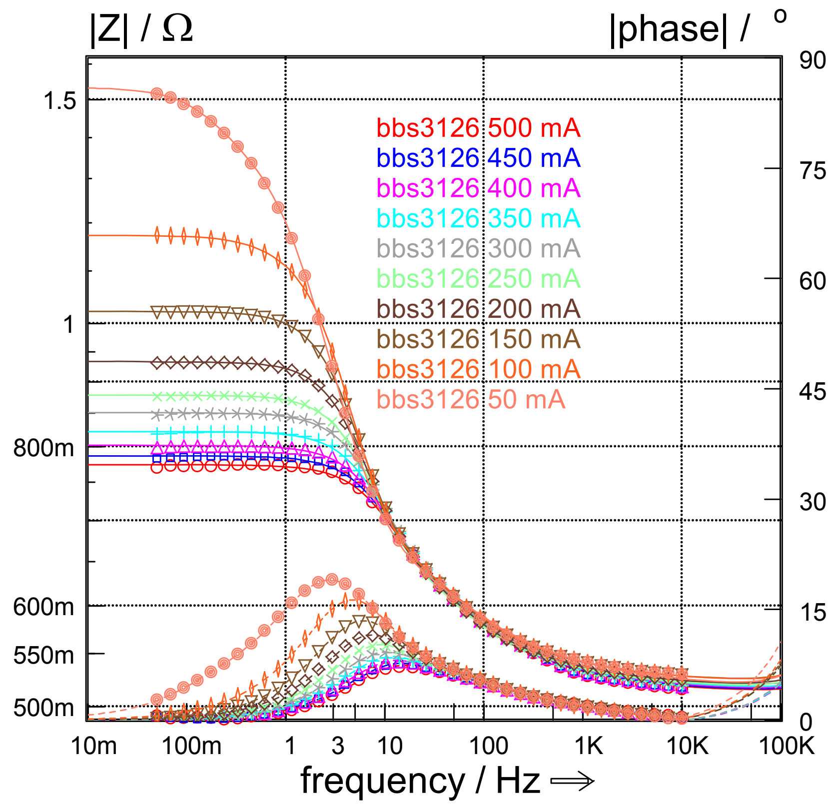
Cathode with ORR
$\mathbf{O_2} + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

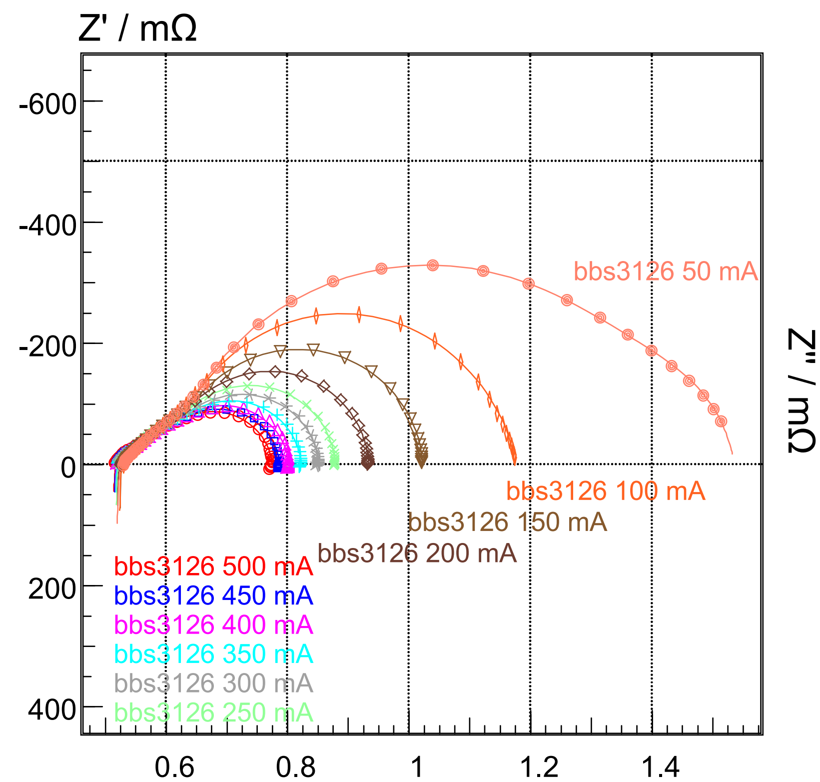
Cathode (conventional)
$4\ H_2O + 4\ e^- \rightarrow 4\ OH^- + 2\ \mathbf{H_2}$




Electrical Circuit
NaOH 30%
(H2O)
Cl2
e-
O2
O2
NaOH
2 H2O
Anode
O -H
H
Na+
Na+
Na+
Na+
O
O-2
OH-
OH-
O-O
O-O
Cl-
Na+
Net
Ag
4 NaOH
NaOH
Membrane
Silver GDE
NaOH 32%
NaCl solution
(Brine)

Impedance Measurements during Oxygen Reduction Reaction (ORR) in 10 N NaOH, on Silver Electrodes at Different Current Densities





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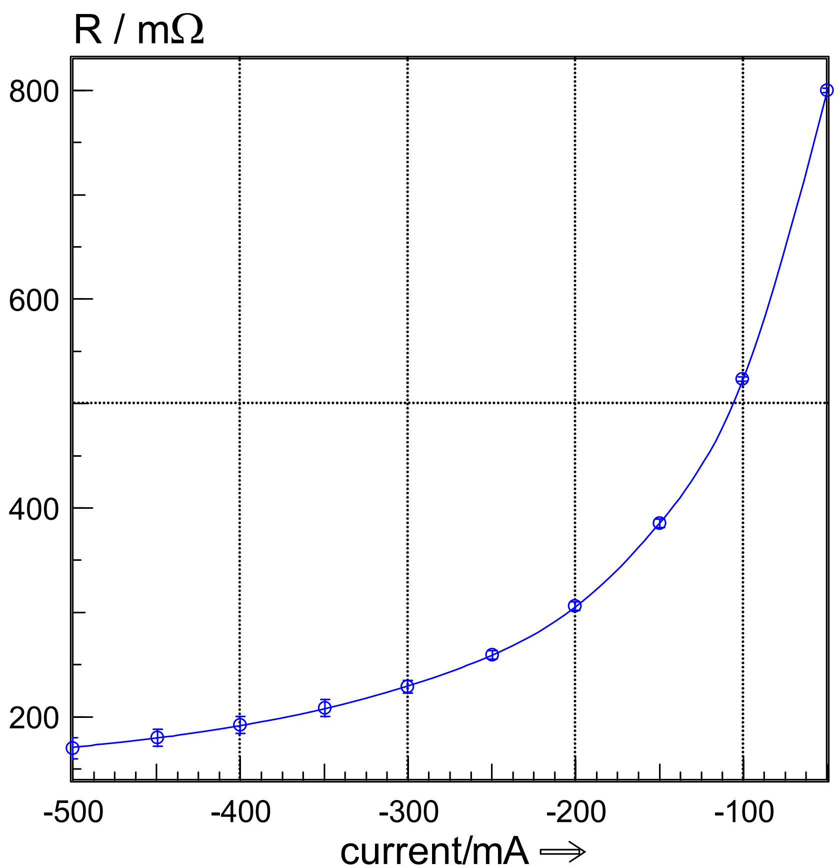
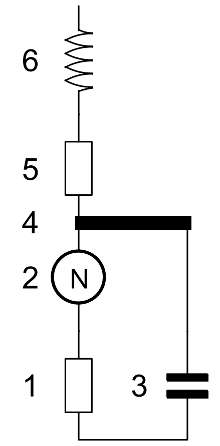
Evaluation of EIS measured during ORR
Equivalent circuit and $R_{ct} = f(i)$



1	170.8	mΩ
2	5.521	$m\Omega \cdot s^{-1/2}$
	19.38	s^{-1}
3	61.37	mF^{α}
	942.8	m
4	1	
	309.9	mΩ
	3.18	mΩ
5	508.6	mΩ
6	73.35	nH



Conclusion

- Determination of the individual potential losses during fuel cell operation
- Determination of degradation mechanism and performance loss
- Improvement of fuel cell performance and stability by understanding instead of trial and error
- Determination of critical operation conditions of fuel cells

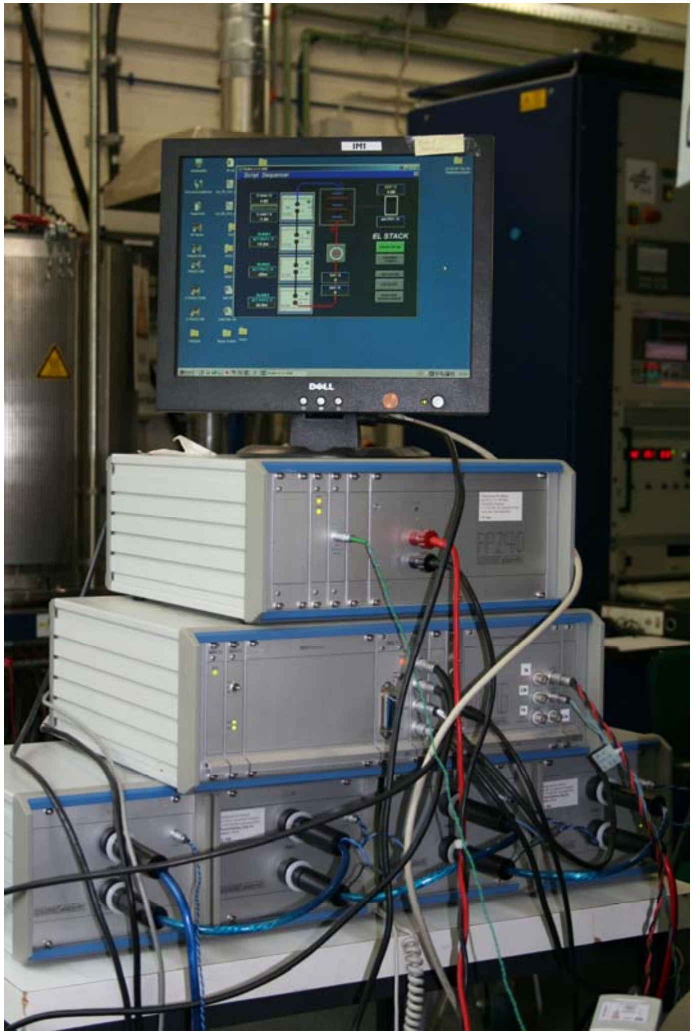
Outlook

- Using the existing models for development and characterization of catalysts and electrodes, optimization of fuel cell structure (flow field, bipolar plate, GDL) Combination and extension of existent and new models

- Application of EIS to fuel cell stacks measurements, simultaneously recording of up to 16 parallel impedance spectra of 16 different cells from the stack

- **EIS on batteries (Li-Sulfur, Li-Air (Metal-Air) for determination of kinetics, degradation, SOC, SOH, BMS**

Experimental EIS set-up for stack measurements



Thank you for the attention!